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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME XIV. SCREENING DETERMINATION OF LEAD IN GASOLINE

D. E. Gilbert, et al

Research Triangle Institute

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME XIV - SCREENING DETERMINATION OF LEAD IN GASOLINE

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This document presents guidelines for developing a quality assurance program for the screening determination of lead in gasoline by the Federal reference method. These guidelines include:

1. Recommended operating practices and techniques,
2. Procedures for assessing performance and qualifying data,
3. Procedures for identifying trouble and improving data quality,
4. Procedures to permit design of auditing activities.

This document is an operations manual, designed for use by operating personnel.

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Prepared for

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ABSTRACT

This document presents guidelines for developing a quality assurance program for the screening determination of lead in gasoline by the Federal reference method. These guidelines include:

1. Recommended operating practices and techniques,
2. Procedures for assessing performance and qualifying data,
3. Procedures for identifying trouble and improving data quality,
4. Procedures to permit design of auditing activities.

This document is an operations manual, designed for use by operating personnel.

This work was submitted in partial fulfillment of Contract Durham 68-02-1234 by Research Triangle Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of February 1975.

SECTION I INTRODUCTION

This document presents guidelines for developing a quality assurance program for the screening determination of lead in gasoline by using a portable colorimeter. This method was published by the Environmental Protection Agency in the Federal Register, November 12, 1974, and is reproduced in appendix A of this document.

This document is divided into four sections:

Section I, Introduction. The Introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual. The Operations Manual sets forth recommended equipment selection, presampling preparation, sampling procedures, data reduction procedures, and sample shipping procedures to insure the collection of data of high quality when contamination is detected.

Section III, Manual for Regional Supervisor. The Manual for Regional Supervisors discusses the assessment of data quality, suggested performance criteria, instructions for quality control checks designed to give an indication or warning that invalid or poor quality data are being collected, and instructions for collecting and analyzing information to identify trouble.

Section IV, Quality Assurance Procedures. The Quality Assurance section presents information relative to the test method, a functional analysis to identify the important operating variables and factors, and statistical properties of and procedures for conducting an independent assessment of data quality.

The objectives of this quality assurance program for the screening of lead in gasoline are to:

1. Provide recommended operating procedures and techniques,
2. Identify and minimize systematic errors to maintain the precision within acceptable limits in the determination process,
3. Provide routine indications of and documentation for satisfactory performance of operating personnel and/or equipment,
4. Provide for prompt detection and correction of conditions which contribute to the collection of poor quality data, and

5. Provide the necessary information to describe the quality of the data.

In order to accomplish these objectives, a quality assurance program must contain the following components:

1. Recommended operating procedures,
2. Routine training of personnel and evaluation of performance of personnel and equipment,
3. Routine monitoring of the variables and parameters which may significantly affect data quality, and
4. Development of statements and evidence to qualify data and detect defects.

Implementation of a quality assurance program will result in data that are more uniform in terms of precision and accuracy. It will enable each monitoring network to continuously generate data that are of acceptable quality.

SECTION II OPERATIONS MANUAL

2.0 GENERAL

This operations manual sets forth recommended operating procedures for the screening determination of lead in gasoline by using a portable colorimeter (ref. 1). This method is reproduced from the Federal Register in appendix A of this document.

This method is intended for use in the field for the quantitative measurement of lead in unleaded gasoline in the range from 2.64 to 26.4 mg Pb/ℓ (0.01 to 0.1 g Pb/gal). This method applies to all commercial gasolines and responds to all types of lead alkyls, as well as to other organic and inorganic forms of lead. This method is a screening test and is not to be used as a replacement for Test for Lead in Gasoline by Atomic Absorption Spectrometry (Federal Register, Vol. 39, No. 131, July 8, 1974).

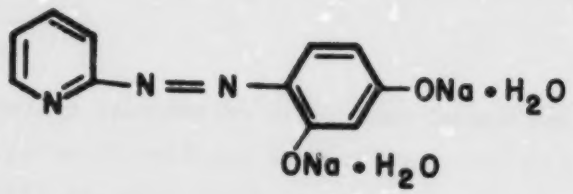
In a brief outline of this method, the gasoline is treated with iodine and tetraethyl ammonium chloride in chloroform and subjected to ultraviolet light. The lead alkyls form water-soluble lead alkyl iodides, which are removed from the gasoline by shaking it with an aqueous ammonium nitrate solution. The aqueous extract is filtered into a solution of 4-(2-pyridylazo)-resorcinol disodium salt (PAR) and ammonium hydroxide. The lead is determined by measuring its PAR complex colorimetrically at 490 nm using a previously prepared calibration curve.

In theory, lead alkyls in gasoline react with halogens to form alkyl lead halides. In the presence of ultraviolet light the lead alkyls react with an iodine/tetraethylammonium chloride/chloroform solution in the following stepwise fashion, with the alkyl lead dihalide R_2PbI_2 being the predominant species formed:

$$R_4Pb + I_2 \rightarrow R_3PbI + RI$$

$$R_3PbI + I_2 \rightarrow R_2PbI_2 + RI.$$

The lead alkyl iodides are water extractable and the solution reacts with the PAR,



to form a red chelate.

PAR also reacts with many other metals forming highly colored complexes. However, none of these are normally found present in a soluble form in gasoline. The following metals were found to form colors with PAR and if present may interfere to give high results: Fe II, Fe III, Co II, Ni II, Cu II, Zn II, Cd II, Mn II, Sm II, V IV, PB II, U VI, Ti IV, and the rare earths.

The accuracy of data obtained from this method depends upon equipment calibration and on the proficiency with which the operator performs his various tasks. This measurement method from reagent preparation through sample analysis and data reporting is a complex operation. Guidelines are presented with special emphasis on quality control checks and decision rules applicable to known problem areas. The operator should make himself familiar with the rules and regulations concerning the reference method as written in the Federal Register (appendix A of this document).

Instructions throughout this document are directed toward on-the-site determinations. A minimum auditing or checking level of one check per calendar week plus any time a gasoline sample is found to approach or exceed the standard for lead in gasoline, i.e., 13.2 mg Pb/ℓ (0.05 g Pb/gal) is recommended (see section 4.2). Sampling period durations and auditing levels are subject to change by the supervisor or manager. Such changes would not alter the basic directions for performing the operation. Also, certain control limits, as given in this manual, represent best estimates for use in the beginning of a quality assurance program and are, therefore, subject to change as field data are collected.

It is assumed that all apparatus satisfies the reference method specifications and that the manufacturer's recommendations will be followed when using a particular instrument (e.g., colorimeter).

EQUIPMENT SELECTION

1. Select the equipment according to specifications given in the reference method (Appendix A) and according to subsection 2.1

2. Perform visual and operational checks of equipment according to subsection 2.1

3. Record new equipment in a receiving record file according to subsection 2.1

CALIBRATION

4. Calibrate the equipment according to subsection 2.2

SAMPLING

5. Sample the gasoline and document it according to subsection 2.3

6. Prepare reagents according to subsection 2.2

7. Analyze samples according to subsection 2.4

8. Validate data by comparing measured value of reference sample to the known value according to subsection 2.4

DATA PROCESSING

9. Perform calculations to determine lead content according to subsection 2.5

10. Report data according to subsection 2.5

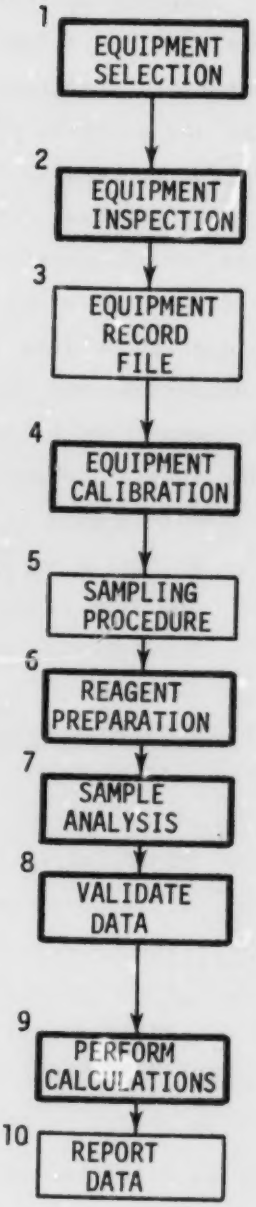


Figure 1. Operational flow chart of the determination process.

The sequence of operations to be performed during each determination period is given in figure 1. Certain operations such as preparation of certain reagents and colorimeter calibration are performed periodically. The remaining operations are performed during each determination period. The operations are classified as equipment selection, presampling preparation, sampling and analysis procedures, and data processing. Each operation or step in the process is identified by a block. Quality checkpoints in the measurement process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other checkpoints involve go/no-go checks and/or subjective judgments by the analyst with proper guidelines for decisionmaking spelled out in the procedures. These operations and checks are discussed sequentially as one progresses step by step through the sequence of actions in figure 1.

The analyst is responsible for maintaining certain records. Specifically, the following log books are maintained:

1. Receiving Record Log Book. This book contains a description of the item received, its serial number or catalog number when appropriate, and results of the acceptance test, signed and dated.
2. Calibration Record Log Book. This book contains the lead calibration curves, standard sample data, and the calibration of all of the equipment.
3. Field Inspection Form Log Book. This book contains the test station sample identification data for each retail station inspected, calculation data, and test results.
4. Sample Shipping Record Log Book. This book contains test station sample identification, test and sample shipping information.

2.1 EQUIPMENT SELECTION

A listing of the required equipment with certain pertinent specifications is given in appendix A. Table 1 contains a supplemental list of sufficient equipment and suppliers. Additional specifications, criteria, or design features are given herein to aid in the procurement of equipment to insure the collection of data of acceptable quality. Also, procedures and limits for acceptance checks of new equipment are presented. A descriptive title and the identification of new equipment should be recorded in the receiving record log book.

Table 1. Equipment and suppliers

Field Sampling Kit; Beckman Instruments Corporation, U. S. Highway 22 at Summit Road, Mountainside, New Jersey.

Refill Packages for the Field Sampling Kit; Beckman Instruments Corporation, U. S. Highway 22 at Summit Road, Mountainside, New Jersey.

Shipping Cartons with Dividers, Tape and Dispenser, Carrolton Products of Alexandria, Virginia.

Shipping Cases for Individual Samples, Improved Mailing Case Co., Wayne, New Jersey.

Flammable Liquid Labels; Association of American Railroads, Bureau of Explosives, Washington, D. C.

Chain of Custody Labels; Forms Office, Environmental Protection Agency, Research Triangle Park, North Carolina.

2.1.1 Field Sampling Kit

2.1.1.1 Specifications. Each kit, shown in figure 2, includes:

Apparatus

1. Ultraviolet lamp, long wavelength, 3660 Å, placed in a standard 4-watt flourescent fixture.

2. A 3-min electric timer connected to the fixture.

3. Measuring block, aluminum, drilled to hold an 18- by 150-mm test tube with a mark at a level equal to 5.0 mℓ of liquid in the test tube.

4. Colorimeter, portable, capable of operating at 490 nm. Any equivalent instrument capable of measurement near 514 nm (the optimum Pb-PAR complex wavelength) may be used. The instrument must be capable of meeting the precision requirements of this method; a repeatability of ±2.64 mg Pb/ℓ (0.01 g Pb/gal) and reproducibility of ±5.28 mg Pb/ℓ (0.02 g Pb/gal)* (see subsection 4.1.2).

5. Test tubes, borosilicate, 18 by 150 mm.

6. Pipets, glass, dropping, capable of delivering 2.0 mℓ with a 2-mℓ bulb.

7. Funnel, plastic, 5 cm (2 in.) inside diameter.

8. Filter paper, ashless, 11.0 cm in diameter, which would allow the organic layer (gasoline/chloroform) to filter through. Whatman 541 or equivalent has been found to be satisfactory.

9. Graduated cylinder, plastic, 10 mℓ.

10. Glass vials, with caps, disposable, 28 g (1-oz) capacity.

Reagents

1. Purity of reagents--Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available (ref. 2). Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

2. Purity of water--Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equal purity.

3. Ammonium hydroxide (sp. gr. 0.90)--concentrated ammonium hydroxide, (NH_4OH).

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*Figure 5 contains a conversion scale and appendix D a conversion factor between mg Pb/ℓ and g Pb/gal. For the remainder of this report mg Pb/ℓ units are used.

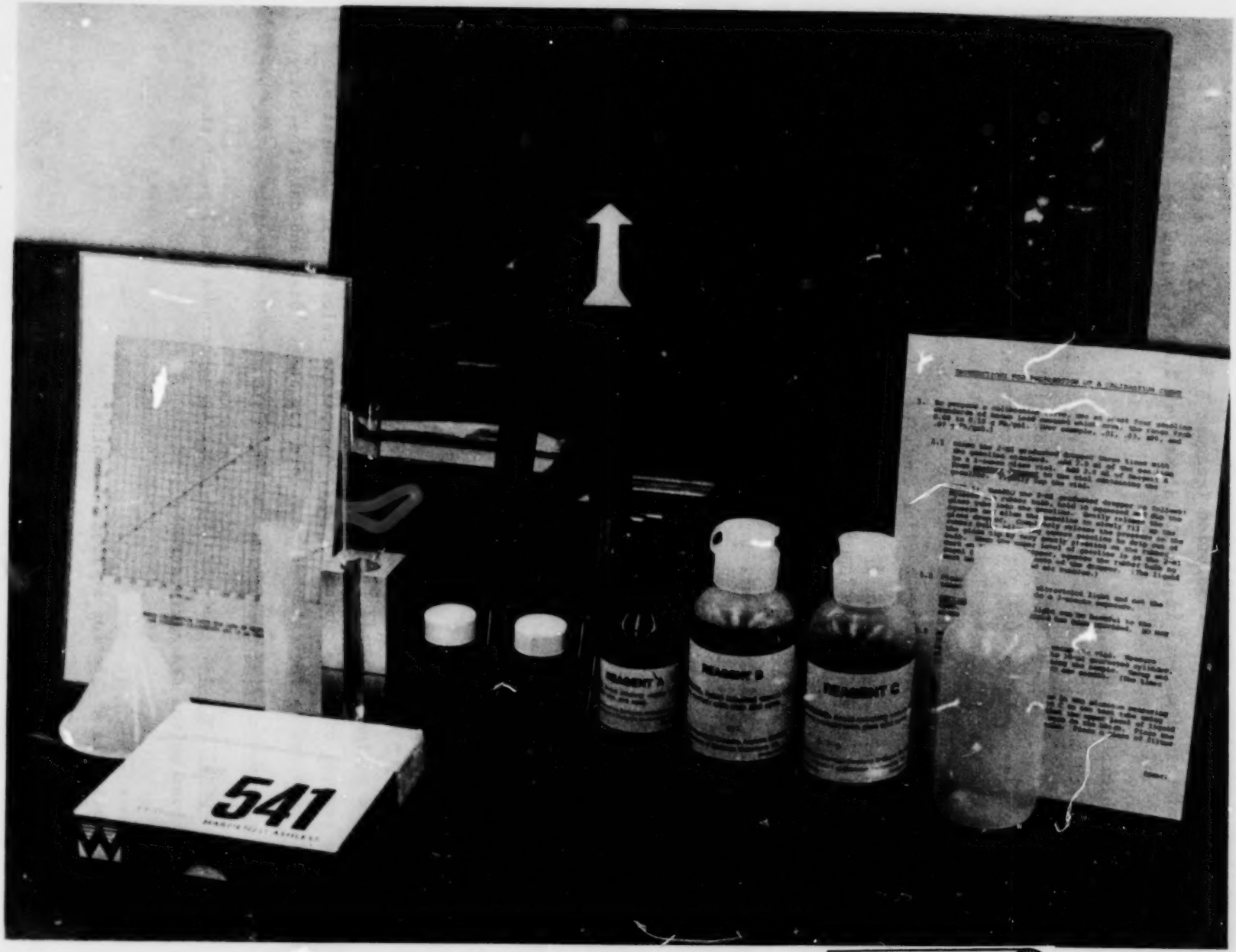

Figure 2. Field sampling kit.

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4. Ammonium nitrate or solution (reagent B)*--15.0 ± 0.1 g of ammonium nitrate dissolved in distilled water in 1.000-ℓ volumetric flask.

5. Chloroform ($CHCl_3$).

6. Disodium salt of 4-(2-pyridylazo)-resorcinol dihydrate (reagent C)*--Dissolve 25.0 ± 0.1 mg of PAR in 750 mℓ of distilled water in a 1.000-ℓ volumetric flask. Add 10.0 ± 0.1 mℓ of concentrated ammonium hydroxide. Dilute to the mark with distilled water. Store this solution in brown bottles in the absence of direct sunlight or in the dark.

7. Gasoline, lead free--Gasoline containing less than 0.26 mg Pb/ℓ.

8. Iodine or iodine/TEAC/$CHCl_3$ solution (reagent A)*, 1.000 g ± 1 mg of iodine and 1000 g ± 1 mg of tetraethylammonium chloride dissolved in a 0.1-ℓ solution of chloroform. Add 1.000 g ±1 mg of tetramethylammonium chloride (TEAC) and mix until dissolved. Dilute to the mark with chloroform.

9. Lead standards--Known amounts of various lead alkyls added to blended unleaded gasoline to cover the range of this method.

10. Tetraethylammonium chloride monohydrate (TEAC).

2.1.1.2 Acceptance Check. Inspect the kit to determine whether all items are included, nothing is broken, and that they conform to the above specifications. The colorimeter should be checked out according to manufacturer's instructions and calibrated according to the instructions set forth in subsection 2.2.

2.1.1.3 Documentation. Record in the receiving record log book a description of the equipment in the field sampling kit, appropriate serial numbers, and the results of the acceptance check, except the colorimetric calibration, which is recorded in the calibration record log book. Sign and date the entry.

2.1.2 Gasoline-Sampling Containers

2.1.2.1 Specifications. The gasoline-sampling containers shall be of the type approved by the EPA administrator.

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*This solution is stable for at least 2 months.

2.1.2.2 Acceptance Check. Inspect the containers for faulty construction, cleanliness, and proper capacity.

2.1.2.3 Documentation. Record in the receiving record log book a description of the containers, supplier, and the results of the acceptance test. Sign and date the entry.

2.1.3 Shipping Cartons and Cases

2.1.3.1 Specifications. The shipping cartons shall contain dividers and be the proper size to facilitate packaging eight sample cans. The cases shall be suitable for packaging individual sample containers.

2.1.3.2 Acceptance Check. Inspect the cartons and cases for damage and suitability for packaging eight cans or individual containers.

2.1.3.3 Documentation. Record in the receiving record log book a description of the cartons, cases, supplier, and the results of the acceptance check.

2.1.4 Chain of Custody Labels

2.1.4.1 Specifications. The chain of custody label shall contain provisions for the Environmental Protection Agency Inspector's Seal, the sample number, date, signature, printed name and title, seal broken by, and date. A copy of a seal is shown in figure 3.

2.1.4.2 Acceptance Check. Inspect the labels to ascertain that they are copies of or contain the same information as shown in figure 3.

2.1.4.3 Documentation. Record in the receiving record log book a description of the labels and the results of the acceptance test.

2.2 PRESAMPLING PREPARATION

2.2.1 Calibration of Colorimeter

The calibration of the colorimeter shall be performed according to the following instructions, using at least a blank (lead-free gasoline) and four working standard samples of known lead content which cover the range from about 0.00 to 20 mg Pb/ℓ. Working standard solutions of gasoline with the above approximate concentrations should be supplied in quantity with certified concentrations by the regional supervisor (section 3.1). They should be stored in brown bottles and kept in the explosion-proof refrigerator except when being used. A blank with four working standard samples

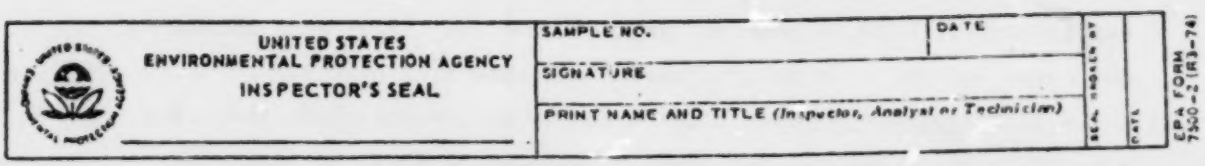

Figure 3. Copy of chain of custody label.

at about 2.6, 7.9, 13.2, and 18.5 mg Pb/ℓ are recommended. Such spacing of the working samples insures acceptable precision of the calibration curve for lead concentrations in the above stated range with maximum precision occuring for concentrations from about 7.9 to 13 mg Pb/ℓ.

1. Rinse the 2-mℓ graduated dropper three times with the standard gasoline solution. Add 2.0 mℓ of the working standard solution to a 28 g (1 oz) glass vial. Using another clean dropper, add 2.0 mℓ of reagent A to the vial containing the working standard solution. Tightly cap the vial.

   NOTE 1: Handle the 2-mℓ graduated dropper as follows: Squeeze the rubber bulb, hold it squeezed and dip the glass tube into the gasoline. Gently relax the squeeze and allow the gasoline to slowly fill up the glass dropper. Completely release the pressure on the rubber bulb; allow any excess gasoline to drip out of the glass tip by very gently pressing on the rubber bulb. When the upper level of gasoline is at the 2-mℓ mark on the glass dropper, squeeze the rubber bulb to expel the entire contents of the dropper into the vial. (The liquid must have no entrapped air bubbles). If gasoline or any of the reagents come into contact with the rubber bulb, discard the bulb and pipet and start again.

2. Place the vial on the ultraviolet light as shown in figure 4 and set the timer to give the sample a 3-minute exposure.

   CAUTION: Ultraviolet light can be harmful to the eyes. A protective shield has been provided. DO NOT remove it or otherwise defeat its purpose. DO NOT stare at the light.

3. After exposure, remove and uncap the vial. Measure 10.0 mℓ of reagent B in a graduated cylinder. Add this to the vial and shake vigorously for 1 minute. (The timer in the kit may be used.)

4. Place a clean 18-mm test tube in the aluminum measuring block. Add 5.0 mℓ of reagent C to the test tube using the mark on the block such that the upper level of liquid in the tube is equal to the mark on the block. Place the plastic funnel in the test tube. Fold a piece of filter paper and place it in the funnel. The filter paper should be rinsed with distilled water prior to

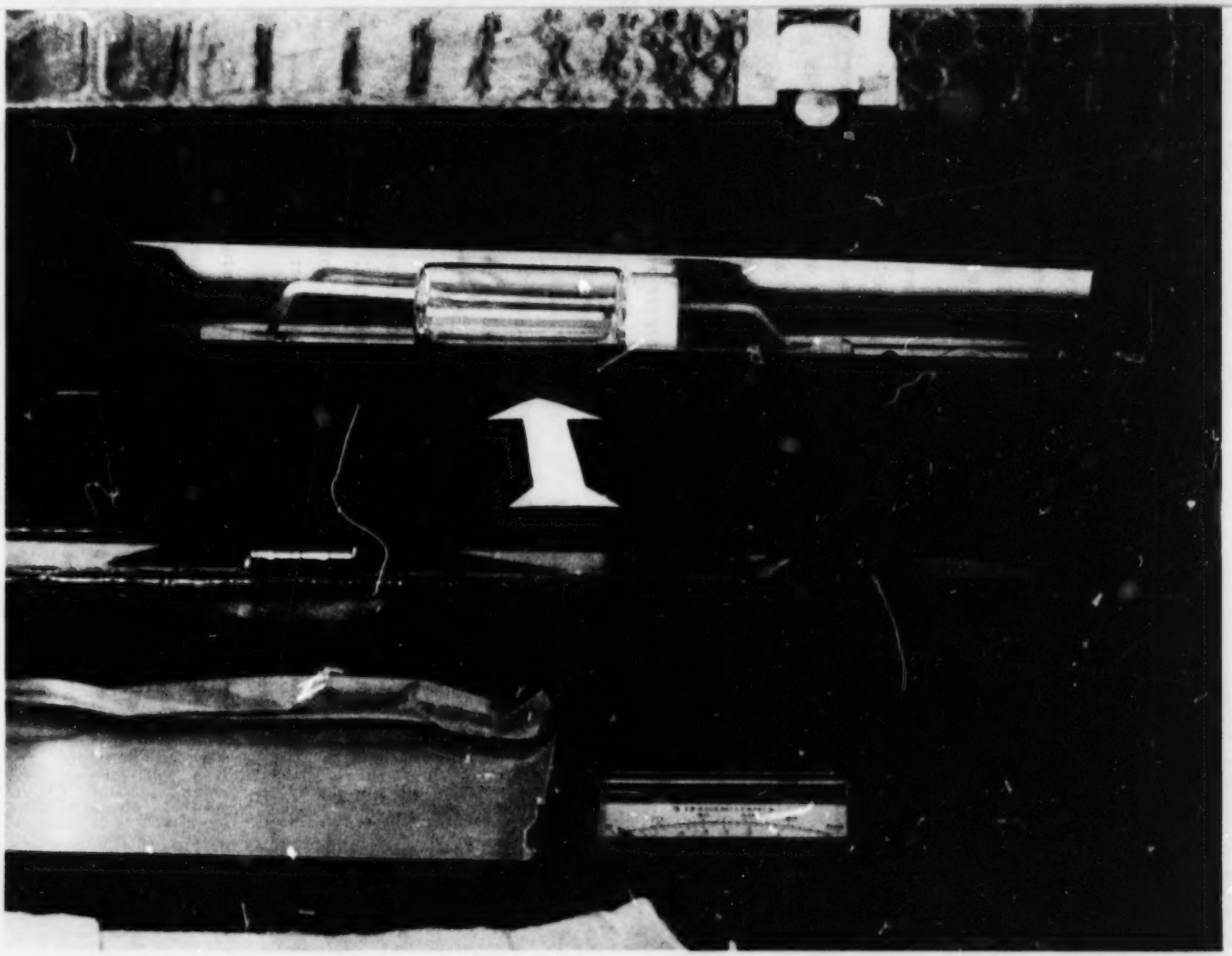

Figure 4. Photograph of the vial positioned on the ultraviolet light.

filtration in order to seal the edges and to prevent migration of the PAR complex up the sides of the filter paper and to prevent breakthough of the filter paper.

5. When the two layers of liquid in the vial have separated, pour the entire contents of the vial into the filter paper. Tap the funnel to add any remaining drops of aqueous solution to the test tube. Remove the funnel and discard its contents. Swirl the test tube gently using a wrist action to obtain a uniform color.

   Note 2: If a few drops of the gasoline layer come through the filter paper, this will not alter the results and can therefore be tolerated. However, if more than 10 drops do come through, refilter the aqueous layer through a fresh filter paper into a clean empty test tube.

   Note 3: Swirling may cause air bubbles to be trapped in the liquid. Wait for these to settle before continuing. Wipe test tube off with a clean lint-free towel to remove any fingerprints that may be present on the surface of the tube.

6. Set the colorimeter at 490 nm. Zero the absorbance scale with distilled water in an 18-mm test tube.

7. Standardize the colorimeter by reading and recording the absorbances obtained with the blank and the working standard samples in 18-mm test tubes.

   Note 4: Time limit--The solution obtained by adding the contents of the vial to reagent C must be read within 10 minutes.

8. Prepare the calibration curve, as shown in figure 5, by plotting the absorbance values versus concentration on rectangular coordinate paper (figure 5 is an example of a calibration curve provided by the manufacturer with 11 data points). Draw a best fit line by eye. Note that the curve does not pass through the origin.

   Note 5: If mg Pb/ℓ are to be used, the abscissa scale should be from 0 to 25 mg Pb/ℓ with the major divisions equivalent to 2.25 mg Pb/ℓ and the smallest divisions equal to 0.5 mg Pb/ℓ.

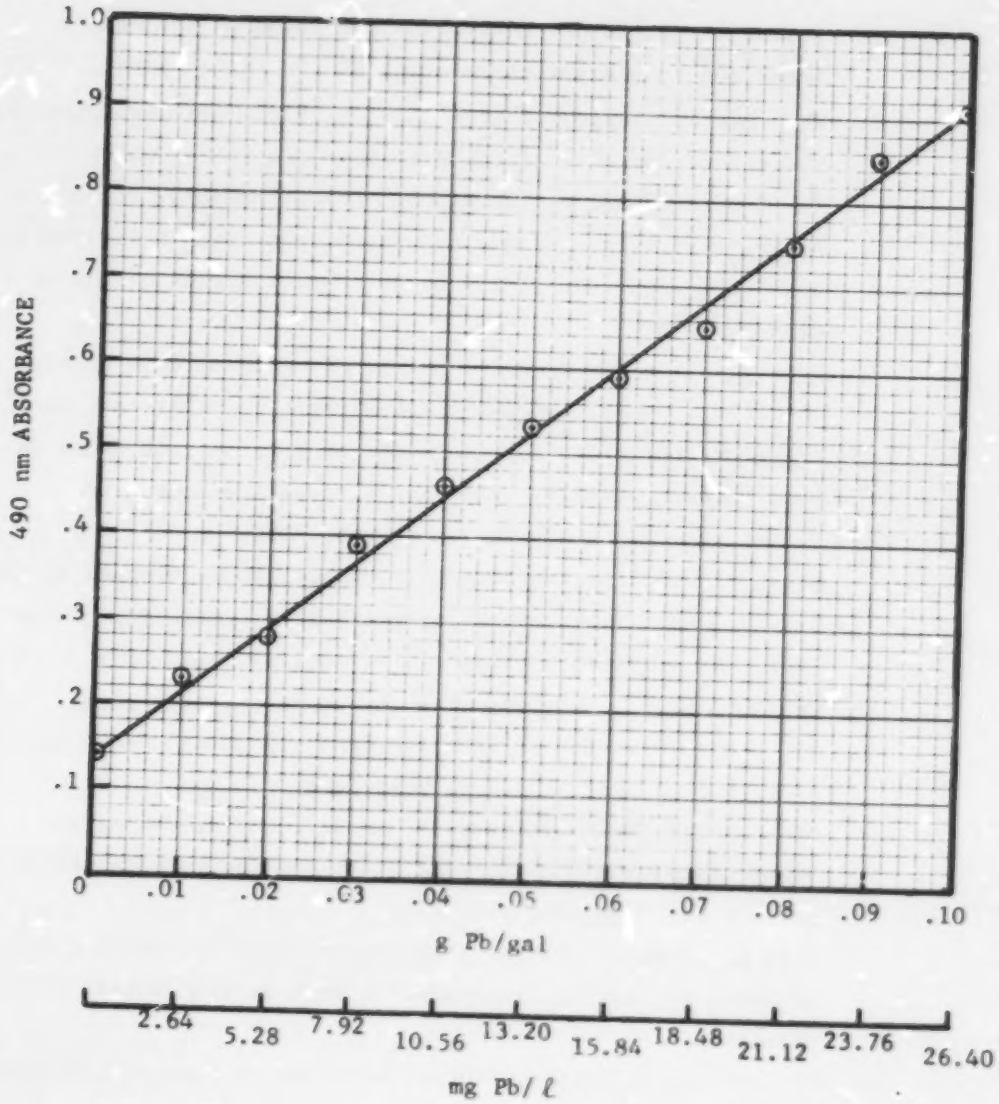

Figure 5. Sample calibration curve for lead in gasoline using the portable colorimeter and 18-mm test tubes.

9. Record, sign, and date the lead calibration curve in the calibration record log book.

2.2.2 Safety Rules

2.2.2.1 Before Test

1. Make sure that all chemicals and equipment needed are available.
2. Prepare only those chemicals and items of equipment actually needed for the test. Check to see that all others are secure in their proper storage locations.

2.2.2.2 In Case of Fire

1. Extinguish it if possible, but do not endanger yourself.
2. Leave the van.
3. Warn anybody in the vicinity of the possible hazard.
4. Call local fire department, if necessary.
5. Call regional headquarters immediately.

2.2.2.3 In Case of an Unusual or Heavy Concentration of Fumes. Leave the van and air it out thoroughly before reentering.

2.2.2.4 General.

1. No smoking or open flames are permitted within or close to the van at any time.
2. All accidents, hazardous occurrences, or potentially hazardous conditions are to be reported to regional headquarters as soon as possible.
3. Minimize amount of gasoline stored in bulk, put excess gasoline in van tank.
4. Immediately wipe up all spills.
5. Maintain the van doors unblocked so that quick exit can be made.
6. Keep samples in refrigerator or explosion-proof cabinet.
7. Pour spent reagents into safety can.
8. Clean van regularly.

2.3 SAMPLING PROCEDURE

2.3.1 Filling Gasoline Sample Containers

Gasoline from a pump labeled to dispense unleaded gasoline should be introduced directly into the sample container described in subsection

2.1.2. A sample of approximately 4 ounces should be taken. The can should be about one-half filled. Under no circumstances should the can be filled above the bottom of the neck of the can. Department of Transportation safety regulations applicable to the shipping of gasoline samples require at least a 5 percent vapor space. Upon taking the sample, the can should immediately be labeled as to date, time, pump serial number, and location of the retail outlet. This information should be recorded in the field inspection form log book as shown in figure 6 and discussed in subsection 2.3.2.

The gasoline retailer should always be paid for the sample taken. If the retailer refuses payment, a signed receipt stating that the gasoline was provided free of charge should be obtained.

If the sample will be analyzed on-site, the can should be loosely capped and taken to the place of analysis. If the analysis is not to be done until later, or if the sample is going to be shipped back to the regional laboratory, the metal seal should be placed over the neck of the can before the cap is screwed tight. A chain of custody label must be attached to all sample cans which are to be shipped. The label attaches to the cap and the sides of the can and will rip upon the attempted removal of either the label or the cap.

2.3.2 Field Inspection Form

The field inspection form shown in figure 6 shall be used to record information about the station as well as test results. The Mobile Source Enforcement Division (MSED) will provide prenumbered forms printed and distributed to each region. The printed forms are in a format which facilitates key punching directly from the form for data collection and storage purposes. An explanation of the field inspection form is presented.

Inspection Numbers--A four-digit (0001 to 9999) number to identify an inspection. This number will also serve as the sample number for chain of custody purposes to be affixed to each sample container which is retained for further testing.

Inspection Number_____

1. Station Information

Station Name:

Brand Name (of Gasoline):_____

Station Address:

Station Owner:

Owner Address:

Station Lessee:

Lessee Address:

Agent In Charge:

2. Invoice Information

Distributor Name:

Distributor Address:

Shipping Point, Name:

Address:

Date of Receipt / /
mo da yr

3. Inspection Information

Date / / Time : Region__
mo da yr hr min

Signs__ Labels___ Nozzles___ Pump Serial Number_____

4. Test Information

Sample / Parameter	Working Standard	Gasoline (first test)	Reference if Applicable		Gasoline* (second test)
Absorbance			Serial Number		
Mg Pb/ℓ					

*Required only if the first test equalled or exceeded the standard.

5. Fuels Inspector

Name: Signature_____

6. Comments

Figure 6. Field inspection form.

1. Station Information--This is information which is used to identify the station and who controls the station. Most of it should be readily available from the station operator.

Station Name: business name of the station; e.g., Main Street Shell.

Station Address: the street address of the service station; e.g., 10016 Main Street, Fairfax, VA 22030.

Station Owner: the name of the person (or company) who owns the retail outlet from which the gasoline is dispensed; e.g., South Arlington Oil Co.

Owner Address: the address of the person (or company) who owns the retail outlet from which the gasoline is dispensed; e.g., 4615 Columbia Pike, Arlington, VA 22202.

Station Lessee: the name of the person (or company), if any, who leases the retail outlet and dispenses gasoline through the facilities; e.g., Thomas Jones (who leases his station from South Arlington Oil Company).

Lessee Address: the legal address of the station lessee; e.g., 10510 Adams Street, Fairfax, VA. 22031.

Agent in Charge: the person who is responsible for the station while the gasoline is being sampled; e.g., Thomas Jones.

2. Invoice Information--This is information which is used to identify the gasoline distributor. It can usually be obtained from the invoice the distributor presents to the retail station operator for gasoline which is delivered.

Distributor Name: the legal name of the distributor; e.g., South Arlington Oil Company.

Distributor Address: the legal address of the distributor; e.g., 4615 Columbia Pike, Arlington, VA. 22207.

Shipping Point Name: name of the terminal from where the gasoline was shipped; e.g., Barcroft Terminal.

Shipping Point Address: address of the terminal from where the gasoline was shipped; e.g., 684 Barcroft Street, Arlington, VA 22206.

Date of Receipt: month, day and year of the latest unleaded gasoline delivery; e.g., 7/1/74.

3. Inspection Information--This is general information about the inspection and items which can be visually checked.

Date: month, day, and year in which the inspection took place; e.g., 7/2/74.

Time: time, by military hours, that the inspection began; e.g., 2:25 PM would be 14:25.

Region: Federal Region in which the inspection took place; e.g., 3.

Signs: a check mark (i.e., ✓) indicates that the retail outlet has the sign required by Section 80.22(d)* of the Federal Register 38, 1254, Jan. 10, 1973, and that it is displayed in the vicinity of each gasoline pump stand as required. If no sign is present or the sign does not comply with the requirements of the regulations, "No" should be entered instead of a check mark, and the violation should be specifically described in the space provided for comments.

Labels: This entry is to be filled out in the same manner as the entry for "signs." Labels should be examined on both unleaded and leaded pumps.

Nozzles: This entry is to be filled out in the same manner as the entry for "signs." Dimensions of nozzles on pumps used to dispense leaded gasoline as well as those on pumps used to dispense unleaded gasoline should be checked.

Pump Serial Number: This is a serial number on the pump. It will usually be located on the hose side of the pump in the vicinity of the hose hanger.

4. Test Information--This provides information concerning the results of the on-site tests for the lead content of gasoline dispensed as unleaded.

Absorbance: This is the meter reading taken directly from the spectrophotometer when the sample (i.e., working standard, gasoline, or reference) whose lead content is to be measured is placed in the instrument.

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*After July 1, 1974, every retailer shall prominently and conspicuously display in the immediate area of each gasoline pump stand the following notice: *Federal law prohibits the introduction of any gasoline containing lead or phosphorus into any motor vehicle labeled "UNLEADED GASOLINE ONLY."* Such notice shall be no smaller than 36-point bold type and shall be located so as to be readily visible to the retailer's employees and customers.

mg Pb/ℓ: This is the lead content of the gasoline sample. It is obtained from a calibration curve which converts absorbance to lead content in milligrams per liter. A working standard sample (13.2 mg Pb/ℓ) is measured before each gasoline sample to verify the calibration curve. A reference sample is measured once a week plus any time a gasoline sample is found to equal or exceed the standard (first test) before remeasuring the gasoline sample (second test).

Pump Meter Reading: This provides the number of cumulative gallons of gasoline dispensed through the pump from which the sample was obtained. The meter is usually located on the face of the pump above the price and gallonage displays for each individual purchase. This reading should only be taken when contaminated gasoline is detected and a stop sale notice is issued.

5. Fuels Inspector

   Name: The last name of the fuels inspector should be printed.

   Signature: The fuels inspector should sign his full name.

6. Comments--This space is provided to allow the fuels inspector to comment on any entry contained on the field inspection form or on other matters deemed relevant to the particular inspection. In all cases where a violation is detected, it should be specifically described in this space.

2.4 ANALYSIS PROCEDURE

A listing of the required steps in sample analysis is given. Recommended quality control practices and safety precautions are also given.

2.4.1 Recommended Quality Control Practices

As part of the analysis procedures, certain checks are recommended for quality control and for data-quality-assessment purposes. Procedures for performing the checks are given along with recommendations for a minimum acceptable frequency for performing the checks. If the checks indicate problems in the analysis of gasoline samples, the frequency of the checks should be increased until the problem is identified and corrective action taken.

To aid in understanding the following discussion, four types of samples referred to in the analysis procedure are defined here. They are:

1. Gasoline sample: A gasoline sample collected in the field for analysis of its Pb content.
2. Blank sample: A working standard sample containing 2.0 mℓ of lead-free gasoline (<0.26 mg Pb/ℓ) and no standard lead solution (see 2.2.1) used to establish the zero or baseline for the colorimeter.
3. Working standard samples: Samples prepared by the inspector from working standard solutions supplied by the regional supervisor with certified concentrations for use as calibration standards.
4. Reference Sample: Samples prepared by the fuel inspector from reference solutions supplied by the Regional Supervisor (prepared in the same manner as the working standard solutions) whose Pb content is accurately known to the supervisor but unknown to the fuel inspector. These samples are used to assess data quality.

The following sequence of analyses is recommended as the minimum level acceptable for quality control and data quality assessment purposes.

1. The colorimeter shall be calibrated (or the manufacturer's calibration curve verified) by measuring a blank and four working standard samples when:
   a. The kit and/or colorimeter is first purchased,
   b. After two weeks of use in the field, or
   c. Any time a working standard sample (or reference sample) can not be measured within ±2.86 mg Pb/ℓ of its known (or true) value.
2. A working standard sample (13.2 mg Pb/ℓ) shall be measured just prior to measuring each gasoline sample. If the measured value of the standard sample is within ±2.86 mg/Pbℓ of the known value, proceed to measure the gasoline sample. If the measured value is outside those limits, all equipment and procedures should be checked and if no problems are found, the colorimeter should be recalibrated as in (1) above.

3. A reference sample, as provided by the regional supervisor (concentration unknown to the analyst or fuel inspector) shall be measured once a week plus any time a gasoline sample is found to equal or exceed the standard for lead in gasoline (i.e., 13.2 mg Pb/ℓ).

2.4.2 Safety Precautions

During the analysis, observe the safety regulations promulgated in subsection 2.2.2 and those presented subsequently.

1. Open and use each chemical or gasoline container only when it is needed during the test. Close it and store it as soon as it has been used.
2. Do not operate electrical switches while working with gasoline.
3. Do not interrupt the test, except for emergency.

2.4.3 Procedure

1. A flow chart of the analysis procedure is given in Figure 7.*
2. Prepare the field sample and a working standard sample containing about 13.2 mg Pb/ℓ in accordance with the directions given in section 2.2.1, steps 2 through 6.
3. Place the test tube containing distilled water in the colorimeter and set the absorbance to zero.
4. Place a test tube containing the working standard sample in the colorimeter and read the absorbance. The analysis of the working standard sample is performed to check the calibration, reagents, and procedures. A record of the calibration check is maintained by plotting the difference between the measured and known values on the Quality Control Chart shown in Figure 8 of section 3.2. Plot the concentrations as read from the calibration curve i.e., to the nearest 0.5 mg Pb/ℓ or 0.002 g Pb/gal. if gallons are used.
5. If the concentration of the standard sample is not determined to within ±2.86 mg Pb/ℓ of its known value, prepare new solutions of reagents and standards, and repeat the calibration procedure. Repeat the analysis of a new working standard sample of about 13.2 mg Pb/ℓ. If the concentration of a working standard sample cannot be determined to within ±2.86 mg Pb/ℓ, notify your supervisor.

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*An unattached 3-page foldout suitable for wall mounting is included in the back of this document.

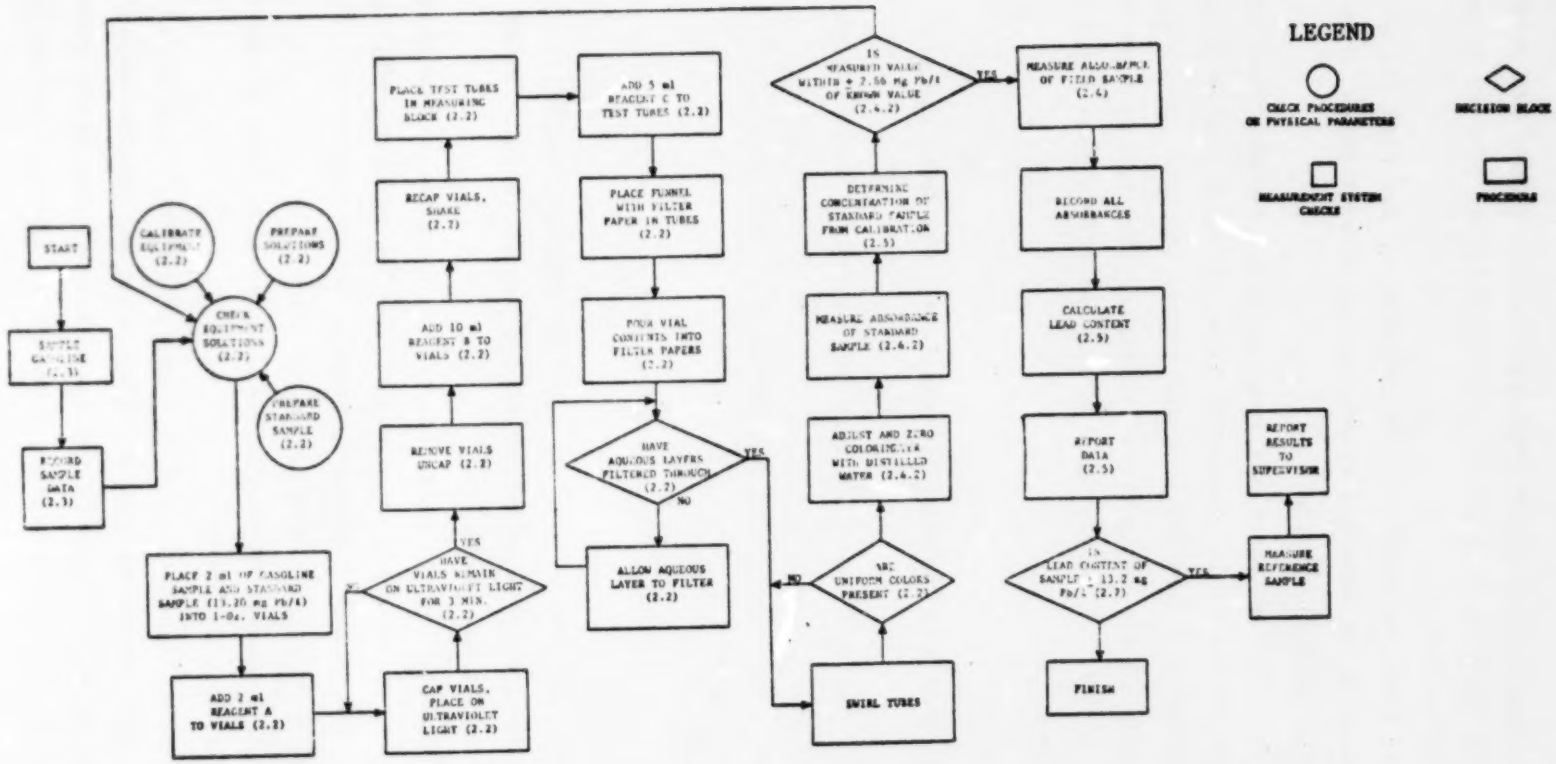

LEGEND
CHECK PROCEDURES OR PHYSICAL PARAMETERS
DECISION BLOCK
MEASUREMENT SYSTEM CHECK
PROCEDURE
START
CALIBRATE EQUIPMENT (2.2)
PREPARE SOLUTIONS (2.2)
CHECK EQUIPMENT SOLUTIONS (2.2)
PREPARE STANDARD SAMPLE (2.2)
SAMPLE GASOLINE (2.3)
RECORD SAMPLE DATA (2.3)
PLACE 2 ml OF GASOLINE SAMPLE AND STANDARD SAMPLE (13.26 mg Pb/l) INTO 1-0z. VIALS
ADD 2 ml REAGENT A TO VIALS (2.2)
CAP VIALS, PLACE ON ULTRAVIOLET LIGHT (2.2)
HAVE VIALS REMAIN ON ULTRAVIOLET LIGHT FOR 3 MIN. (2.2)
YES
REMOVE VIALS UNCAP (2.2)
ADD 10 ml REAGENT B TO VIALS (2.2)
RECAP VIALS, SHAKE (2.2)
PLACE TEST TUBES IN MEASURING BLOCK (2.2)
ADD 5 ml REAGENT C TO TEST TUBES (2.2)
PLACE FUNNEL WITH FILTER PAPER IN TUBES (2.2)
POUR VIAL CONTENTS INTO FILTER PAPERS (2.2)
HAVE AQUEOUS LAYERS FILTERED THROUGH (2.2)
YES
NO
ALLOW AQUEOUS LAYER TO FILTER (2.2)
ARE UNIFORM COLORS PRESENT (2.2)
NO
YES
SWIRL TUBES
ADJUST AND ZERO COLORIMETER WITH DISTILLED WATER (2.6.2)
MEASURE ABSORBANCE OF STANDARD SAMPLE (2.6.2)
DETERMINE CONCENTRATION OF STANDARD SAMPLE FROM CALIBRATION (2.5)
IS MEASURED VALUE WITHIN ± 2.66 mg Pb/l OF KNOWN VALUE (2.6.2)
YES
MEASURE ABSORBANCE OF FIELD SAMPLE (2.6)
RECORD ALL ABSORBANCES
CALCULATE LEAD CONTENT (2.9)
REPORT DATA (2.5)
IS LEAD CONTENT OF SAMPLE ≥ 13.2 mg Pb/l (2.9)
YES
FINISH
REPORT RESULTS TO SUPERVISOR
MEASURE REFERENCE SAMPLE

Figure 7. Flow chart for the analysis of lead in gasoline.

If the concentration of the working standard sample was determined to within ±2.86 mg Pb/ℓ of its certified value, proceed to analyze the gasoline sample.

6. Place the gasoline sample in the colorimeter and read the absorbance.

Note 6: The solution obtained by adding the aqueous phase to reagent C must be read within 10 minutes.

7. Record the absorbances of all samples (i.e., working standard and gasoline) on the field inspection form, shown in figure 6, in the field inspection form log book and record the working standard sample data in the calibration record log book and plot on the quality control chart provided by the supervisor (see figure 8 in section 3.2).

2.4.4 After Analysis

1. Make sure that all chemical and gasoline containers are well closed.
2. Make sure that all items are securely stored in their assigned van locations.
3. Wash hands thoroughly after everything has been stored.

2.5 DATA REDUCTION

1. From the calibration curve, find the lead content of the gasoline sample.

   a. Report the lead content of gasoline samples rounded to the nearest 1 mg Pb/ℓ value (or to the nearest 0.01 g Pb/gal if these units are used).

   b. For quality control purposes and for establishing or checking calibration curves determinations of working standard samples and reference samples should be rounded to the nearest 0.1 mg Pb/ℓ (or 0.001 g Pb/gal if these units are used).

2. Record the lead content on the Field Inspection Form in the Field Inspection Form Log Book.
3. If the concentration of lead in a gasoline sample exceeds 13.2 mg Pb/ℓ, proceed to section 2.7 after this section is completed.
4. A summary of the results of the field inspections in the form of copies of the Field Inspection Form (or as directed by the super-

visor) should be sent to the Monitoring Source Enforcement Department in Washington, D.C. at weekly intervals.

Note 7: The reference method (subsection 7.4 of appendix A) recommends rounding to the nearest 0.01 g Pb/gal (2.64 mg Pb/ℓ) however, for simplicity, it is recommended that gasoline sample determinations be rounded to the nearest 1 mg Pb/ℓ for reporting.

2.6 SAMPLE SHIPPING PROCEDURE

1. Fuels inspectors are required to ship the required number of gasoline samples for phosphorus determination and any sample that exceeds the standard for lead to the regional laboratory for analysis. Two kinds of shipping packages as well as two methods of shipment are available.

2. Single samples may be sent in individual shipping canisters. The shipping canister is designed to hold one 8-ounce sample can. The canister is closed by a metal screw-on lid.

3. Shipping cartons designed to hold a total of eight sample cans may be used to ship groups of samples. These shipping cartons have been sent to the regions in a collapsed form and must be assembled before use. The cartons should be opened up and the bottom flaps sealed with the tape which is provided. A layer of absorbent material should always be placed on the bottom of the box. The absorbent material is packaged sheetwise in rolls. One sheet is sufficient to cover the bottom of the box, run up the side, and fit over the top of the cans. Dividers must be used to separate the cans. After the cans are placed in the box, the remaining absorbent material is placed over the cans and the top flaps should be folded down and sealed with tape. A red "Flammable Liquid" label should be placed on the shipping carton or canister.

4. The packages can be shipped either by United Parcel Service (UPS) or Railroad Express Agency (REA). UPS operates in all states but Alaska, Arizona, Hawaii, Idaho, Montana, Nevada, and Utah. In these states, REA can be used. UPS is preferred since it is the less costly service. A package can be shipped by UPS at a cost of less than $1, while those shipped by REA may cost over $10.

5. To ship the packages, the name and address of the receiving laboratory should be written on a label which should then be attached to the shipping carton or canister. Labels are preferred since the cartons and canisters can be used more than once. For shipment by means of UPS, a "Hazardous Materials" label is required. The label should be filled out as follows:

Full Shipping Name of Article - Unleaded Gasoline For Analysis

Classification - Flammable Liquid Red Label

Weight or Volume - _____ 8 Oz. Cans

Type D.O.T. Label Required - None

Shipping charges should be paid at the time the package is delivered to the forewarding company for shipment.

2.7 PROCEDURE WHEN CONTAMINATION IS DETECTED

When the concentration of lead exceeds 13.2 mg Pb/ℓ, the gasoline is contaminated. In which case, proceed as follows.

1. Take another gasoline sample after flushing the nozzle and hose by pumping one gallon of gasoline from the retailer's hose spout into a waste receptacle. Immediately fill the sample can completely, rinse, then dump the sample into a clean waste receptacle in the same manner as the original one gallon. Immediately fill this same sample can half full, cap and transport it to the van for analysis.
2. Dispose of the waste material by pouring it into a gasoline tank.
3. Analyze in sequential order a working standard sample, a reference sample, and the new gasoline sample according to the instructions in subsections 2.4 and 2.5. Record the serial number of the reference sample on the Field Inspection Form.
4. Record the results of the analyses on the Field Inspection Form Log Book.
5. If the concentration of lead in the gasoline exceeds 13.2 mg Pb/ℓ, report the results of the gasoline and reference samples to your supervisor. If your supervisor authorizes issuance of notice of violation of the Federal Standard for lead, proceed according to

his instructions or as follows: (a) place a notice of contamination on the pump, prohibiting the sale of gasoline and to each unleaded pump supplied by the storage tank from which samples were obtained, (b) record on the Field Inspection Form in the Field Inspection Form Log Book the cumulative gallonage reading on the meter of each pump to which a notice of contamination has been applied, (c) instruct the retailer regarding procedures to follow to have the notice of contamination removed, (d) provide the retailer with forms for removal of notice (i.e., notice of disposition or cure and notice of satisfactory test results.), (e) send the remaining gasoline sample to the regional laboratory, and report the issuance of the contamination notice to the Regional Office.

SECTION III MANUAL FOR REGIONAL SUPERVISOR

3.0 GENERAL

The term "supervisor" as used in this document applies to the individual in charge of a field team. He is directly responsible for the validity and the quality of the field data collected by his team.

It is the responsibility of the supervisor to identify sources of uncertainty or error in the determination process for specific situations and, if possible, to eliminate or minimize them by applying appropriate quality control procedures to insure that the data collected are of acceptable quality. These guidelines cannot cover all possible situations; therefore, it is important for the supervisor to make full use of his experience and knowledge to insure the collection of data of acceptable quality. Specific actions and operations required of the supervisor for a viable quality assurance program include, but are not limited to, the following:

1. Monitor/Control Data Quality
   a) Direct the Field Inspector in performing field tests according to the proceudres given in the Operations Manual.
   b) Perform or qualify results of the quality control checks (i.e., insure that checks are valid).
   c) Perform necessary calculations and compare quality control checks with suggested performance criteria.
   d) Make corrections or alter operations when suggested performance criteria are exceeded.
   e) Forward qualified data for additional internal review or to user.
2. Routine Operations
   a) Provide and maintain the Field Inspector with an adequate supply of working standard solutions with accurately known lead concentrations for calibration purposes.
   b) Obtain from fuel inspectors immediate reports of suspicious data or malfunctions. Initiate corrective action or, if

necessary, specify special checks to determine the trouble; then take corrective action. Document corrective action taken.

c) Examine the Inspector's log books periodically for completeness and adherence to operating procedures.

d) Approve Field Inspection Form and calibration sheets for filing.

3. Evaluation of Operations

a) Evaluate available alternative(s) for accomplishing a given objective in light of experience and needs.

b) Evaluate Inspector training/instructional needs for specific operations.

Insuring satisfactory data quality on a day-by-day basis with the inspector in the field and the supervisor in the regional office requires the application of quality assurance techniques by the inspector with rigorous monitoring and guidance from the supervisor.

Specific quality assurance procedures recommended for implementation by the supervisor are:

1. Provide the inspector with a supply of certified working standard solutions for colorimeter calibration and calibration checks.
2. Provide the inspector with a quality control chart for plotting the differences in the measured and certified values of working standard samples along with the necessary guidelines for:
   a) Judging when the data are of acceptable quality.
   b) Judging when the data are not of acceptable quality and corrective action is required.
   c) Interpreting data patterns on the control chart to identify likely causes of excess variability and/or biases.

Preparation and certification of working standard solutions and the construction and use of a control chart for differences in measured and known values of those solutions are discussed in the following two subsections. The third subsection titled Suggested Performance Criteria summarizes the criteria used throughout this document, and gives the reasoning used and assumptions made in arriving at the criteria.

3.1 PREPARATION OF CERTIFIED WORKING STANDARD SOLUTIONS

Working standard solutions should be purchased or prepared and certified by the regional laboratory and supplied to the field inspector by his supervisor. The working standard solutions can be prepared by addition of leaded gasoline (or lead alkyls) to blended unleaded gasoline.

Note 8: The standard reference material for lead in gasoline obtainable from the National Bureau of Standards can not be utilized for this screening method because a reference fuel (91 volume percent 2,2,4-trimethylpentane and 9 volume percent n-heptane) rather than gasoline is used as the substrate fuel and does not achieve the same response from the colorimeter as does gasoline.

The following procedure is recommended

1. Purchase quantities of blended unleaded gasoline and leaded gasoline from a reputable distributor.
2. Determine the lead content of both gasolines by atomic absorption spectrometry (if lead concentrations are provided by the distributor use them).
3. Prepare a minimum of 4 working standard solutions with lead concentrations near 2.6, 7.9, 13, and 18 mg Pb/ℓ determining the approximate required volume of leaded gasoline using the following relationship.

$$V_1 = V_T \left(\frac{Pb_s - Pb_{ul}}{Pb_1 - Pb_{ul}} \right) \qquad (1)$$

where

V_1 = Required volume of leaded gasoline to prepare a standard sample with a concentration of Pb_s, mℓ.

V_T = Total volume of the working standard sample being prepared, mℓ.

Pb_s = The desired concentration of the working standard sample (i.e., either 2.6, 7.9, 13, or 18), mg Pb/ℓ.

Pb_{ul} = The lead concentration of unleaded gasoline from 2 above, mg Pb/ℓ.

Pb_1 = The lead concentration of the leaded gasoline from 2 above, mg Pb/ℓ.

4. Based on preparing a total volume of 1 liter (V_T) of a working standard solution place the volume of leaded gasoline (V_1) as cal-

culated from equation 1 into a 1 liter volumetric flask. Add unleaded gasoline to bring the volume to the 1 liter mark.

Note 9: The required volume of each working standard solution will depend upon the inspector's schedule and will have to be estimated by the supervisor. Generally a liter of each working standard should last about 2 weeks assuming an average of eight analyses per day.

5. After preparation, each of the working standard solutions should be analyzed a minimum of four times extending over a 2-day period (i.e., two replicates per day) by atomic absorption spectrometry. A range (i.e., the largest minus the smallest) of ≤ 2.2 mg Pb/ℓ for the four analyses indicates acceptable precision and the average of the four analyses is used as the certified lead concentration of the working standard solution. The remaining working standard solution should be placed in a container suitable for shipping and storage with the date of analysis, certified concentration, and analyst's name affixed in some semipermanent manner. If the range is > 2.2 mg Pb/ℓ the equipment, reagents, and procedures should be checked, corrective action taken, and four additional analyses performed until the range criteria is satisfied.

   Note 10: The variance of atomic absorption measurements is approximately one fourth the variance of the screening method. Therefore, four replications by atomic absorption should reduce the variance in the certified value of the working standard solution to 1/16 or a negligible fraction of the variance associated with the screening method determinations.

6. The inspector should be provided with an adequate supply of working standard solutions at all times.

3.2 CONSTRUCTION AND USE OF A CONTROL CHART

A quality control chart for plotting the differences between the measured and certified values of working standard samples provides a visual check of the present calibration, a chronological record of data quality, a corrective action record when the determination process is out of control, and it may be used to identify trouble areas. The recommended control

chart is shown in figure 8. It is assumed that the difference in measured and certified values is normally distributed about a zero mean. Limits for the control chart were calculated using the repeatability standard deviation, i.e., $\sigma_r = 0.953$ mg Pb/ℓ for the reference method. Action limits are defined as the $\pm 3\sigma_r$ values and warning limits are set at $\pm 2\sigma_r$ values. The assumptions made in setting these limits are discussed in subsection 3.3.

Each time a working standard sample is measured the inspector should calculate the difference (d) by always subtracting the certified value (Pb') from the measured value (Pb), maintaining the positive or negative sign for d. Each difference is plotted on the control chart and connected to the previously plotted point with a straight line.

The filled-in control charts should be forwarded to the supervisor for his review at the end of each week in the field.

3.2.1 Use of the Control Chart to Estimate Data Quality

For any given time period, e.g., one calendar month or quarter, if all the points (i.e., differences) on the control chart are within the action limits and somewhat randomly distributed about the center line or 0, it can be assumed that the precision of the field measurements for that time period is consistent with the precision (repeatability) of the reference method as given in 7.1.1 of appendix A.

Under these conditions the lead in gasoline determinations can be reported with $\pm$ 3 sigma limits as

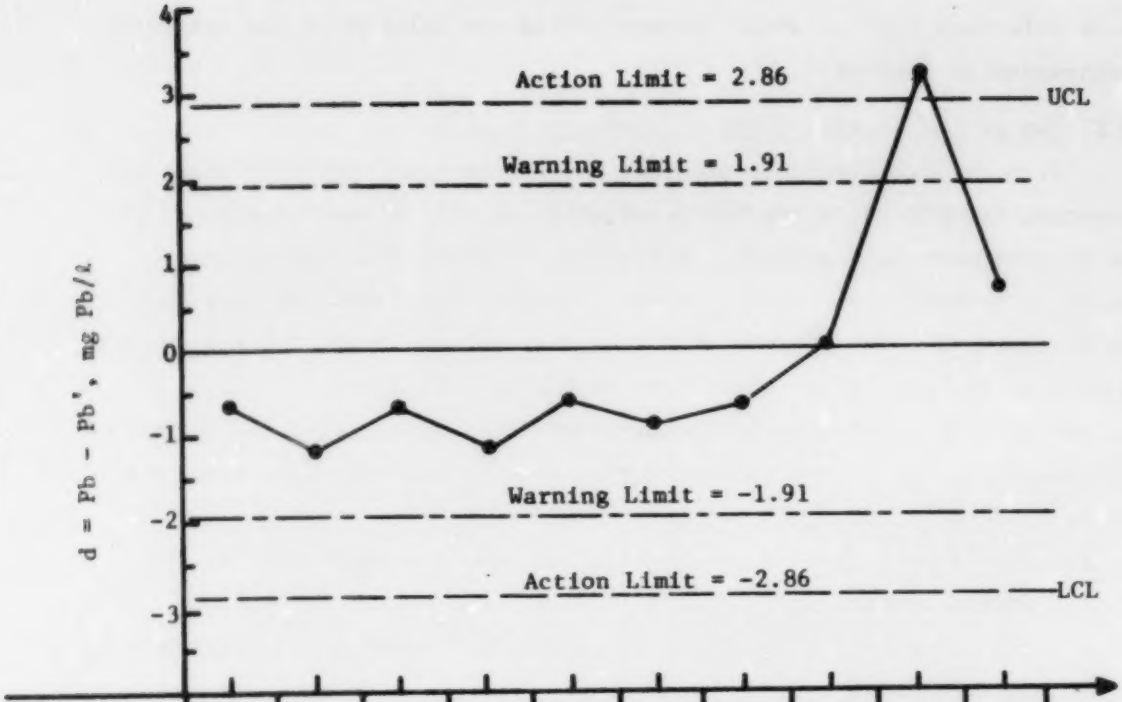
$$Pb \pm 2.86 \text{ mg Pb/ℓ}$$

where

Pb = The measured lead concentration of the gasoline sample, mg Pb/ℓ.

2.86 = $3\sigma_r$ (see subsection 4.1.1), mg Pb/ℓ.

The utility of the above statement follows from the fact that if the determined values of Pb are normally distributed about a true value Pb_T (assuming no bias) with $\sigma\{Pb\} = 0.953$ mg Pb/ℓ, then on the average the true value Pb_T will be contained in the internal as constructed above approximately 99.7 percent of the time. An exact confidence statement is dependent on the number of measurements used in estimating $\sigma\{Pb\}$. The



CHECK NO.	1	2	3	4	5	6	7	8	9	10
DATE	2/19/75	2/20/75	2/21/75	2/24/75	2/25/75	2/26/75	2/27/75 9 a.m.	2/27/75 11 a.m.	2/28/75 9:30 a.m.	2/28/75 10:30 a.m.
ANALYST	F.S.	F.S.	F.S.	F.S.	F.S.	F.S.	F.S.	F.S.	F.S.	F.S.
PROBLEM AND CORRECTIVE ACTION							Bias indicated by Tennelec negative points. Multipoint calibration performed.		Error in preceding Aqueity 2 run working standard sample was prepared last analysis.	

Figure 8. Quality control chart for checking the calibration curve.

above estimate was made from 57 measurements. As more data are obtained for estimating $\sigma\{Pb\}$ the percent confidence will approach 99.7. This statement is about precision; to estimate bias or accuracy requires the use of reference samples whose concentrations are unknown to the inspector as discussed in section 4.3.

3.2.2 Use of the Control Chart to Identify Trouble

In a quality assurance program, one of the most effective means of preventing trouble is to respond immediately to indications of suspicious data or equipment malfunctions. One means of assuring a fast reaction time is to provide the inspector with objective guidelines for judging when the determination process is out of control and corrective actions are required or when it is in control and should be left alone.

The following criteria are recommended for judgeing when the determination process is out of control, requiring trouble shooting and corrective action:

1. Anytime one plotted point (i.e., difference) falls outside the action limits.
2. Two out of three consectutive points fall between the warning and action limits.
3. Seven consecutive points fall on the same side of the mean or zero line.

Further analysis of gasoline samples should not be attempted until the cause is determined, corrected, and documented (on the control chart).

Indications of the source of trouble may, in some cases, be revealed by the pattern of the plotted points on the control chart. For example, exceeding the first or second criteria with all the previously plotted points showing a random scatter within acceptable limits indicates a somewhat sudden shift in data quality. This could be the result of:

1. A sudden malfunction of the colorimeter,
2. A recently contaminated reagent,
3. A deviation (either on purpose or accidently) from the standard operating procedures,
4. A mistake in colorimeter reading or in the conversion from absorbance to concentration.

Trouble shooting should take the form of visually checking the equipment for obvious malfunctions, checking the colorimeter by zeroing the absorbance scale using distilled water, visually checking the reagents for signs of contamination, and reviewing the operating procedures.

Exceeding the third criterion indicates that a systematic error (bias) has developed in the measurement process. How critical this error is depends on the magnitude of the shift and on the sequential pattern of the plotted points. A trend indicating a bias as large as the standard deviation of the method should be a signal to locate and correct the cause before continuing to analyze gasoline samples. However, seven consecutive points falling on the same side of but very close to the center line would not be cause for interrupting the measurement of gasoline samples.

3.3 SUGGESTED PERFORMANCE CRITERIA

Performance criteria as suggested herein are based on the premise that measurement precision consistent with that stated for the reference method (see section 7 of appendix A) is acceptable and that measurements exhibiting larger imprecision should be prevented and/or detected and eliminated with high probability. In arriving at the performance criteria as discussed in the ensuing subsections, the following subjects had to be addressed:

1. The measure of precision to be used in calculating acceptable limits, i.e., repeatability, reproducibility or some value between these two extremes.
2. Uncertainty in the calibration curve.
3. The criteria for judging acceptable performance, i.e., should action limits be set at $\pm$ 2 sigma or $\pm$ 3 sigma levels.
4. The minimum auditing level necessary to assess and document the precision and accuracy of the lead in gasoline determinations.
5. The required frequency of measuring working standard samples to verify the calibration curve.

The above subject areas are discussed in the ensuring subsections in the same order as listed above.

3.3.1 Measure of Precision

Precision is a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. The conditions under which the working standard samples will be measured by the field inspector are: 1) different sample i.e., different working standard samples prepared from a homogeneous working standard solution; 2) same specimen i.e., homogeneous working standard solution. 3) same analyst; 4) same equipment; 5) different days; and 6) same laboratory.

Under these conditions it is felt that the repeatability standard deviation, σ_r, (see section 4.1.2) is the appropriate measure of precision to use in setting criteria for judging acceptable performance. A repeatability standard deviation of σ_r = 0.953 mg Pb/ℓ as calculated from the value given in section 7.1.1 or appendix A for repeatability is used throughout this document. This assumes that the statistic, σ_r, calculated from 57 data points (ref. 1) is a good estimate of the population parameter σ_r and that it contains components of variability from:

1. Replication error,
2. Scatter of data points about a particular calibration curve,
3. Variability among calibration curves.

The validity of these assumptions and of the use of σ_r in setting limits must be checked and adjustments made, if necessary, when sufficient field data become available, e.g., 50 or so determinations of working standard solutions as reported by the field inspector.

3.3.2 Uncertainty in the Calibration Curve

There are two sources of error associated with the calibration curve. One source of error is the scatter of the data points about the calibration line. The second source of error is the uncertainty of the calibration curve, i.e., the variability between calibration curves. In setting action limits on the control chart of figure 8 and in recommending that a blank and four upscale points are sufficient for verifying the calibration curve the following assumptions were made:

1. That σ_r is known and is equal to 0.953 mg Pb/ℓ.

2. That the colorimeter calibration curve provided by the manufacturer is generated from a minimum of 11 data points and that future multipoint calibrations by the field inspector act to reduce the uncertainty in the calibration curve and does not in essence generate a new curve each time.

Based on a calibration curve fit to N data points, the correct standard deviation to use in calculating the control chart limits and tolerance intervals for future calibration checks is (see ref. 4 for a discussion of tolerance limits):

$$\sigma^1 = \sigma_r \left[\frac{N+1}{N} + \frac{(Pb_o - \overline{Pb})^2}{\sum_{j=1}^{N} (Pb_j - \overline{Pb})^2} \right]^{1/2} \qquad (2)$$

where

σ^1 = the standard deviation for future measurements with an N point calibration curve, mg Pb/ℓ.

σ_r = known repeatability standard deviation, mg Pb/ℓ.

N = number of data points used to fit the calibration curve, dimensionless.

Pb_o = lead concentration point on the abscissa about which the tolerance limit is set, mg Pb/ℓ.

Pb_j = lead concentration of the j^{th} calibration point, mg Pb/ℓ.

$\overline{Pb}$ = average lead concentration of all calibration points i.e., $1/N \sum_{j=1}^{N} Pb_j$, mg Pb/ℓ.

From the above relationship, it is seen that for the case where $Pb_o = \overline{Pb}$ the relationship becomes

$$\sigma^1 = \sigma_r \left[\frac{N+1}{N} \right]^{1/2} . \qquad (3)$$

For N = 11, in the case of the manufacturers calibration curve, $\sigma^1 = 1.04\ \sigma_r$, and as the field inspector continues to check and adjust the calibration curve N increases and σ^1 approaches σ_r fairly rapidly. Therefore, the use of σ_r in setting control limits seems appropriate, especially once the determination kit has been in use for a period of time.

If in practice the calibration curve shifts significantly from calibration to calibration and an excessive number of determinations of standard working samples are falling outside the action limits on the control chart, the supervisor should either:

1. Provide the field inspector with additional standard working solutions in the concentration range of interest for developing calibration curves,
2. Keep using the same number of standard working solutions to develop the calibration curve but broaden the action limits by multiplying the present ones by

$$\left[\frac{N+1}{N}\right]^{1/2} = \left[\frac{6}{5}\right]^{1/2} = 1.1.$$

Recommending a minimum number of five points for checking/verifying the calibration curve on a once-a-week basis is based on engineering judgement. Due to the relatively large normal variability of the process (repeatability is $\pm$ 20 percent for lead concentrations close to the standard) it is felt that any number less than about five points could lead to unwarranted shifting of the calibration curve by the field inspector.

3.3.3 Criteria for Judging Acceptable Performance

The three criteria given in section 3.2.2 for detecting trouble; namely, 1) anytime one point falls outside the action limits, 2) anytime two of three consecutive points fall between the warning and action limits, and 2) anytime seven consecutive points fall on the same side of the center line; are recommended as reasonable criteria for judging acceptable performance.

The probability of any one of the three criteria being exceed while the determination process is actually operating properly, i.e., the process is in control, is approximately 0.05. Such criteria should prevent unnecessary tinkering with the process when it is actually in control and at the same time insure precision of measurements consistent with the reference method.

3.3.4 Minimum Auditing Level

Performance auditing in the form of providing the inspector with blind samples (i.e., reference samples with concentrations known to the

supervisor/auditor but unknown to the inspector) for periodic determinations serves as a check on the quality of the field measurements and can be used as a proficiency evaluation of the operator.

The minimum auditing level recommended for this program is that the inspector analyze a reference sample once a week (while in the field) and anytime a gasoline sample is found to equal or exceed the standard for lead in gasoline, i.e., 13.2 mg Pb/ℓ.

Such an auditing scheme is recommended because 1) if all the gasoline samples measured are well below the standard, a minimum auditing level of once a week should be sufficient to assess and document data quality, and 2) by measuring a reference sample each time a gasoline sample is found to equal or exceed the standard will provide an independent verification of the measurement process each time enforcement action has to be taken.

The auditing scheme is designed to maximize confidence in determinations where the lead concentration equals or exceeds the standard.

3.3.5 Frequency of Calibration Checks as Quality Control Checks

The recommended frequency of measuring working standard samples to verify the calibration curve given here is based on the assumption that gasoline samples will be analyzed on site. That is, it is assumed that the mobile laboratory will be driven to the gasoline station for the check. Under these conditions it is felt that the calibration curve should be verified before analysis of each gasoline sample. However, if in practice several gasoline samples are collected and brought to the laboratory for analysis it may be sufficient to verify the calibration before and after each analysis cycle or 4-hour analysis period, whichever is shorter.

SECTION IV QUALITY ASSURANCE PROCEDURES

4.0 GENERAL

The control of data quality is a function of two related activities of the quality assurance program: (1) development of standard operating procedures including control limits, and (2) assurance of conformance to the procedures and control limits. Standard operating procedures and control limits are recommended in the operations manual of this document. It is emphasized that if the field inspector conscientiously adheres to the procedures and checks of section II, then the precision and accuracy of the lead determinations should be within acceptable limits. Assurance of data quality basically involves collecting the information necessary to document and demonstrate the quality of the measured data. This section of the document will discuss the activities necessary to document and demonstrate data quality.

Verification of data quality is important in this instance because the data generated by this method are to be used to determine if the standard for lead in gasoline is being met. If results indicate that the standard is being exceeded the appropriate enforcement group will be required to take action. Thus, the professional competence of the field inspector, the operating procedures used, and the measured values that he reports may be challenged in legal proceedings.

The quality assurance procedures presented in this section should be carried out or closely monitored by the individual directly responsible for the quality of the reported data. In each laboratory one individual should be assigned the responsibility for quality assurance.

The purposes of this section are to:

1. present information relative to the measurement method (i.e., a functional analysis) to identify the important operations and factors,
2. present an independent performance audit procedure for use in quantifying data quality on an interlaboratory basis,
3. present techniques for data quality assessment.

These three purposes will be discussed in the order stated in the subsections that follow. The first subsection (3.1) will contain a functional analysis

of the measurement method with the objective of identifying the most important factors that affect the quality of the reported data and of estimating the expected variation and biases in the determination resulting from equipment and field inspector errors.

Subsection 4.2 contains a discussion of an independent performance audit. Such and audit involves the fuel inspector analyzing a reference sample (i.e., NBS or otherwise certified samples) when the field sample exceeds the value of the lead content promulgated in the Federal Register. Since the fuel inspector is required as part of his normal operation to forward a certain percentage of the gasoline samples to the Regional Laboratory for phosphorus determinations, an alternative auditing procedure could be for the laboratory to analyze these gasoline samples by atomic absorption for lead and to compare this value to the fuel inspector's value. Such an audit, if feasible, could serve as an independent check of the determination process from sample handling through the final calculations. It would provide a means of assessing data quality as a function of bias and precision and serve as an independent verification of data quality for future users of the data.

Data quality assessment is discussed in subsection 4.3. A method for estimating the precision and accuracy of the reported data using the results from the independent performance audit is given. Also, a method of testing the quality against given standards using sampling by variables is given.

4.1 FUNCTIONAL ANALYSIS OF THE FIELD TEST METHOD

The determination of lead in gasoline requires a sequence of operations and measurements that yields as an end result a number that serves to represent the mass of lead in a unit volume of gasoline. The degree of agreement between the measured and the true value of a sample can be estimated from the agreement between measured and standard or reference values. Precision and accuracy of the determination process are reduced to or maintained within acceptable limits by identifying and, where feasible, eliminating systematic errors. The importance of a variable on the precision or accuracy of a determination process is a function of the variable mean value and variance, how it is related to the dependent variable, and its probability of occurrance under normal operating conditions.

The objectives of this subsection are to:

1. Evaluate variables and estimate error ranges,
2. Through a variance analysis determine the variability to expect in the determination of lead in gasoline.
3. Through a bias analysis estimate the expected bias, if any in the determination of lead in gasoline.

A functional analysis of the determination process is performed to determine all the operations and variables that may affect the quality of the reported measurements. Data quality is characterized by measures of precision and bias. In subsection 4.1.1 variables believed to be important to the measurement method are discussed. Estimates of the mean, variance, and probability distribution are made using data from published reports when available, and using engineering judgement or intuition when documented data are not available. These data are then used in a variance analysis (subsection 4.1.2) to determine the resulting variability of the measured value i.e., the mass of lead per unit volume of gasoline. The data from subsection 4.1.1 are also used in subsection 4.1.3 to estimate the potential bias of the determination process.

4.1.1 Variable Evaluation and Error Range Estimates

The milligrams of lead per liter of sample is determined from comparison with the calibration curve. The calibration curve is constructed from standard samples supplied by the Regional Laboratory. The Regional Laboratory determines the concentration of the standard samples according to the atomic absorption spectrometric method promulgated in the Federal Register, July 8, 1974.

The error sources then can be grouped according to whether they originate in the determination of the concentrations of the standard samples or of the gasoline samples.

4.1.1.1 Potential Errors in Determining Concentrations of Standard Samples

The potential errors in the determination of concentrations of standard samples are expounded in detail in another document (ref. 3). In that document it has been promulgated that the precision in the determination of lead concentrations of gasoline samples by atomic absorption expressed as the repeatability standard deviation is $\pm$ 0.48 mg Pb/ℓ. For the present

functional analysis, this value of the precision represents the potential error in the determination of the concentrations of working standard solutions and reference samples. Also, it is recommended that at least 4 determinations by A.A. be made thus the standard deviation of the mean should be 0.48/2 = 0.24 mg Pb/ℓ.

4.1.1.2 Potential Errors in Determining Concentrations of Total Lead. The quantity of lead in a sample at the time of collection can differ from the measured value due to:

1. Contamination during sampling, handling and analysis.
2. Incomplete color development from the use of poor reagents or lack of mixing.
3. Errors in the preparation of the calibration curve.
4. Inprecision of the colorimeter and reading errors.
5. Measurement error in the volumes of gasoline sample and reagents.
6. Evaporization losses during analysis.

There are no data available for estimating the error associated with each of the above operations. However, a judgement can be made from the values given for repeatability and reproducibility of the method as written in the Federal Register (see appendix A).

The repeatability and reproducibility of the measurement method at the 95 percent confidence level are given as 2.64 mg Pb/ℓ and 5.28 mg Pb/ℓ, respectively. The above values mean that on the average duplicate results should agree within ±2.64 mg Pb/ℓ 95 percent of the time when the determination process is operating properly. Also, results of two laboratories measuring the same sample should agree within 5.28 mg Pb/ℓ 95 percent of the time when both laboratory determination processes are in control.

It is felt that at least half of the difference in the repeatability and reproducibility values is due to variability in analyst technique in performing the above listed items (3), (4), and (5).

The sources of variability listed in items (1), (2) and (3) are estimated to account for less than half of the total measurement process variability. The errors introduced by items (3) and (4) over a long period of time would tend to be randomly distributed about a zero mean. Incomplete color development acts as a negative bias and sample contamination and evaporization during analysis would act as a positive bias.

4.1.2 Variance Analysis

Many different factors may contribute to the variability of a measurement method, for example:

1. The analyst,
2. Apparatus and reagents used,
3. Equipment calibration,
4. The environment (temperature, humidity, etc.)

The variability will be larger when the measurements to be compared are performed by different analysts or with different equipment, than when they are carried out by a single analyst using the same equipment. Many different measures of variability are conceivable according to the circumstances under which the measurements are performed.

Only two extreme situations will be discussed here. They are:

1. Repeatability, r, is the value below which the absolute difference between duplicate results, i.e. two-determinations made on the same sample by the same analyst using the same equipment over a short interval of time, may be expected to fall with a 95 percent probability. This represents the best precision that could be achieved on an interlaboratory basis.
2. Reproducibility, R, is the value below which the absolute difference between two measurements made on the same sample by different analysts in different laboratories using different equipment may be expected to fall with a 95 percent probability. This is representative of intralaboratory precision.

The above definitions are based on a statistical model according to which each determination is the sum of three components:

$$Pb = \bar{P}b + b + e \qquad (4)$$

where

Pb = the determined value, mg Pb/ℓ,

$\bar{P}$ = the general average or accepted value of the sample, mg Pb/ℓ.

b = an error term representing the differences between laboratories, mg P/ℓ

e = a random error occurring in each determination, mg Pb/ℓ.

In general b can be considered as the sum

$$b = b_r + b_s \tag{5}$$

where b_r is a random component and b_s a systematic component. The term b is considered to be constant during any series of measurements performed under repeatable conditions, but to behave as a random variate in a series of measurements performed under reproducible conditions. Its variance is denoted by

$$\text{var } b = \sigma_L^2 \tag{6}$$

where σ_L^2 is the variance between laboratories, including the variance between analysts and between equipment.

The term e represents a random error occurring in each measurement. Its variance is denoted by

$$\text{var } e = \sigma_r^2, \tag{7}$$

where σ_r^2 is called the repeatability variance.

For the above model the repeatability, r and the reproducibility, R, are given by (ref. 5)

$$r = 1.960\sqrt{2\,\sigma_r^2} = 2.77\,\sigma_r \tag{8}$$

and

$$R = 1.960\sqrt{\sigma_r^2 + \sigma_L^2} = 2.77\,\sigma_R\,, \tag{9}$$

where 1.960 is the value of the Student's equal-tails t-distribution for an infinite number of degrees of freedom at the 95% confidence level, and σ_R^2 is the reproducibility variance, i.e., the population variance under reproducibility conditions.

Values of σ_r and σ_R can be obtained from the values of repeatability and reproducibility respectively as given for the reference method in the

Federal Register (see Appendix A). The repeatability r, is given as 2.64 mg Pb/ℓ. Using this value in equation (8) gives σ_r = 0.953 mg Pb/ℓ. Reproducibility is given as R = 5.28 mg Pb/ℓ then from equation (9) σ_R = 1.91 mg Pb/ℓ.

As can be seen the reproducibility standard deviation is larger than the repeatability standard deviation by a factor of 2. It is felt this difference is due primarily to differences in analyst techniques.

The determined value of Pb can be expressed phenomonologically as

$$Pb = Pb_S/V_T \tag{10}$$

where Pb_S represents the quantity of lead in the gasoline sample and V_T represents the volume of the solution in the test tube at the time of analysis, i.e.

$$V_T = V_S + V_A + V_B + V_C \tag{11}$$

where V_S, V_A, V_B and V_C are the volumes of gasoline sample, reagent A reagent B, and reagent C, respectively, added to the test tube.

Using equation (10) the dependence on or variation of Pb with Pb_S and V_T will be analyzed. The coefficient of variation of Pb, CV{Pb}, (ref. 4) is given by

$$CV\{Pb\} = \sigma\{Pb\}/Pb = \sqrt{(\sigma\{Pb_s\}/\ Pb_s)^2 + (\sigma\{V_T\}/V_T)^2} \tag{12}$$

where $\sigma\{V_T\} = \sqrt{\sigma^2\{V_s\} + \sigma^2\{V_A\} + \sigma^2\{V_B\} + \sigma^2\{V_C\}}$,

and the standard deviation of Pb is given by

$$\sigma\{Pb\} = CV\{Pb\} \times Pb, \tag{13}$$

Equation (12) was derived by differentiating implicitly the natural logarithm of equation (10), squaring both sides and substituting $\sigma\{Pb\}/\ Pb$ and $\sigma\{V_T\}/V_T$ for dPb/Pb and dV_T/V_T respectively. This derivation assumes that the variables Pb_s and V_T are uncorrelated.

For this analysis, it is assumed that the variation in the quantity of lead in the gasoline sample is due to the variability of the colorimeter.

This variability should be relatively small, on the order of $\sigma\{Pb_S\}$ = 0.264 mg Pb/ℓ, which is only one tenth of the repeatability. Taking Pb = 13.2 mg Pb/ℓ, $\sigma\{Pb\} = \sigma_r$ = 0.953 mg Pb/ℓ and V_T = 19 mℓ, then

$$CV\{Pb\} = \sigma\{Pb\}/Pb = 0.072, \tag{14}$$

$$CV\{Pb_S\} = \sigma\{Pb_S\}/ Pb_S = 0.02, \tag{15}$$

$$CV\{V_T\} = \sqrt{CV^2\{Pb\} - CV^2\{Pb_S\}} = 0.069 \tag{16}$$

and

$$\sigma\{V_T\} = CV\{V_T\} \times V_T = 1.3 \text{ mℓ}. \tag{17}$$

From this analysis, it is obvious that control actions should be directed toward measuring the volumes of sample and reagents as the most effective means of controlling and assuring data of acceptable quality. If greater precision than that given for the reference method is desired by the supervisor it is recommended that pipets (2 mℓ) capable of greater precision be used. Such pipet could be one that has the 2 mℓ mark on a small capillary such that a small reading error would not greatly influence the accuracy of the total volume.

4.1.3 Bias Analysis

There are no data available for estimating the bias of the measurement process. The bias can be evaluated by measuring reference samples as recommended in section 4.2.

Assuming that the true or acceptable value, Pb_T, of a sample is known, then from equation (4)

$$\bar{Pb} - Pb_T = \tau \tag{18}$$

which represents the bias of the measurement method. An estimate of the bias can be obtained from audit results as discussed in section 4.2.

4.2 PROCEDURES FOR PERFORMING A QUALITY AUDIT

If implemented properly an independent audit can be used to evaluate the total determination process through the use of reference samples or

if more convenient and desirable comparison of the fuel inspectors determination with that obtained by atomic absorption analysis of gasoline samples sent to the Regional Laboratory for phosphorus determination. A reference sample is defined as a gasoline sample whose lead content is accurately known (preferably NBS certified) to the auditors but unknown to the analyst being audited. Results of an audit provide an independent assessment of data quality by providing a means of estimating the precision and bias of the reported results.

4.2.1 Procedure for performing a Quality Audit

The individual or organization responsible for performing the audit should obtain a supply of gasoline samples with known lead concentrations (see section 3.1). Samples should be placed in sample containers identical to the containers used in the field. Each container should contain an identification number which uniquely labels that container. A "lot" of reference samples representative of the range of concentrations used to prepare the calibration curve should be shipped or delivered to the fuel inspector or analysis laboratory.

4.2.2 Frequency of Audit

The optimum frequency of audit is a function of certain costs and the desired level of confidence in the data quality assessment. Also, another consideration would have to be the quality of the data presently being reported. However, there are no data available to estimate the bias of the method and this could be important to the accuracy of the reported data.

Initially an auditing level on once a week plus anytime a gasoline sample is analyzed that equals or exceeds the federal standard for lead in gasoline is recommended. For an analyst analyzing about 8 samples a day this would result in a minimum of 13 audits per calendar quarter. The maximum audit level would be a function of how many gasoline samples were found to equal or exceed the standard. Also, the fuel inspector is measuring a working standard sample before analyzing each gasoline sample. These data may also be used in assessing data quality.

4.3 DATA QUALITY ASSESSMENT

Two aspects of data quality assessment are considered in this section. The first considers a means of estimating the precision and accuracy of the reported data, e.g., reporting the bias, if any, and the standard deviation associated with the measurements. The second consideration is that of testing the data quality against given standards using sampling by variables. For example, lower and upper limits, L and U, may be selected to include a large percentage of the measurements and outside of which it is desired to control the percentage of measurements to, say, less than 10 percent. If the data quality is not consistent with these limits, L and U then, action is taken to correct the possible deficiency as quickly as possible and to correct the previous data when possible or feasible.

4.3.1 Estimating the Precision and Accuracy of the Reported Data

This section will indicate how the audit data collected in accordance with the procedure described in Section 4.2.1 will be utilized to estimate the precision and accuracy of the determination of interest. The audit data results in a collection of differences between known values of lead and the measured values. The difference d_j is given by

$$d_j = Pb_j - Pb_{T_j} \tag{19}$$

where Pb_j = Determined value of lead in the reference sample, mg Pb/ℓ,

Pb_{T_j} = True or known value of lead in the reference sample, mg Pb/ℓ, and

j = the audit number, $j = 1, \ldots n$.

Let the mean and standard deviation of the differences d_j, $j = 1, \ldots n$ audits, be denoted by $\bar{d}$ and s_d, respectively. Thus,

$$\bar{d} = \sum_{j=1}^{n} d_j/n \tag{20}$$

and

$$s_d = \left[\sum_{j=1}^{n} (d_j - \bar{d})^2/(n-1) \right]^{1/2} . \tag{21}$$

4.3.2 Statistical Tests

The mean $\bar{d}$ is an estimate of the relative bias in the measurements (i.e., relative to the known or accepted value). Assuming the audit value to be unbiased, the existence of a bias in the laboratory data can be checked by the Student's equal-tails t-distribution (ref. 5)

$$t_{n-1} = \frac{\bar{d} - \mu}{s_d/\sqrt{n}} \qquad (22)$$

where μ is the population mean which is assumed to be zero.

If t is significantly large in absolute value, i.e., greater than the tabulated value of t with n - 1 degrees of freedom, which is exceeded by chance only 5 percent of the time, then the bias is considered to be real and some check should be made for a possible cause of the bias. If t is not significantly large, then the bias should be considered zero or negligible. However, in either case, its calculated value will be reported with the laboratory data for that audit period.

The standard deviation, s_d, is a function of both the standard deviation of the field and of precision with which the reference sample value is known. Assuming reference sample values are known with much greater precision (see section 3.1) than the field laboratory measurements then the calculated s_d is an estimate of the standard deviation of the field laboratory measurements. Table 2 contains a sample calculation of $\bar{d}$ and s_d, for a sample size with eleven degrees of freedom.

The calculated standard deviation can be checked against the assumption made in subsection 4.1.2 concerning σ {Pb} = σ_r = 0.953 mg Pb/ℓ, under repeatability conditions. The calculated standard deviation, s_d, is checked against the assumed value, σ_r, by using the one-sided χ^2 test for σ in a normal distribution,

$$\frac{\chi^2}{f} = \frac{s_d^2}{\sigma^2\{Pb\}}, \qquad (23)$$

where χ^2/f is the statistic for the value of a random variable having the chi-square distribution with f = n - 1 degrees of freedom. If χ^2/f is larger than the tabulated value exceeded only 5 percent of the time, then

Table 2. Computation of mean difference, $\bar{d}$, and standard deviation of differences, s_d

General formulas $d = Pb_j - Pb_{T_j}$		Specific example data (mg Pb/ℓ)	
d_1	d_1^2	-0.5	0.36
d_2	d_2^2	-1.2	1.44
d_3	d_3^2	+1.8	3.24
d_4	d_4^2	-1.2	1.44
d_5	d_5^2	-2.0	4.0
d_6	d_6^2	+0.3	0.09
d_7	d_7^2	-1.4	1.96
d_8	d_8^2	+0.3	0.09
d_9	d_9^2	-2.0	4.0
d_{10}	d_{10}^2	-1.0	1.0
d_{11}	d_{11}^2	+0.6	0.36
d_{12}	d_{12}^2	-1.1	1.21
Σd_j	Σd_j^2	-7.5	19.19
$\bar{d} = \Sigma d_j / n$		$\bar{d} = -0.63$	
$s_d^2 = \frac{\Sigma d_j^2 - (\Sigma d_j)^2/n}{n-1}$		$s_d^2 = 1.32$	
$s_d = \sqrt{s_d^2}$		$s_d = 1.15$ mg Pb/ℓ	

it would be concluded that the test procedure is yielding results with more variability than is acceptable due to some assignable cause of large variation.

The determined values should be reported along with the estimated bias, $\bar{d} = \tau$, the standard deviation, s_d, the number of audits, n, and the total number of determination periods (number of days analyses were performed) N. Estimates, i.e., s_d and $\bar{d}$, which are significantly different from the assumed population parameters should be identified on the data sheet. For example, based on the data of table 2, if the analyst reported a value of Pb = 10.3 mg Pb/ℓ for one of the N field tests not audited, then that measurement would be reported as

1. Measured value, Pb = 10.3 mg Pb/ℓ
2. Calculated bias, $\bar{d} = \hat{\tau} = -0.63$ mg P/ℓ
3. Calculated standard deviation, $\hat{\sigma}\{Pb\} = s_d = 1.15$ mg Pb/ℓ
4. Auditing level, n = 12, N = 65.

From the above data, users of the data can calculate confidence limits appropriate to what the data are to be used for.

The t-test and χ^2-test described above are used to check on the biases and standard deviations separately. In order to check on the overall data quality as measured by the percent of determination deviations outside prescribed limits, it is necessary to use the approach described below.

4.3.3 Sampling by Variables

Because the lot size (i.e., the number of determination periods during a particular period, normally a calendar quarter) is small, N = 65, and consequently, the sample size is small on the order of n = 13, it is important to consider a sampling by variables approach to assess the data quality with respect to prescribed limits. That is, it is desired to make as much use of the data as possible. In the variables approach, the means and standard deviations of the sample of n audits are used in making a decision concerning the data quality.

Some background concerning the assumptions and the methodology is repeated below for convenience. However, one is referred to one of a number of publications having information on sampling by variables; e.g.,

see references 5-9. The discussion below will treat the specific problem herein which has some unique features as compared with the usual variable sampling plans.

The difference between the analyst-measured and the known value of lead is designated as d_j, and the mean difference over n audits by $\bar{d}$, that is,

$$\bar{d} = \frac{1}{n} \sum_{j=1}^{n} (Pb_j - Pb_{T_j}). \qquad (24)$$

Theoretically, Pb_j and Pb_{T_j} should be measures of the same lead concentration, and their difference should have a mean of zero on the average. In addition, their differences should have a standard deviation approximately equal to that associated with measurements of Pb separately.

Since the standard deviation is known $\sigma(Pb) = 0.953$ mg Pb/ℓ the lower and upper limits, L and U, respectively, outside of which it is desired to control the proportion of differences, d_j, are defined by three standard deviations. The values of the lower and upper limits are $-3(0.953) = -2.86$ mg Pb/ℓ and $3(0.953) = 2.86$ mg Pb/ℓ, respectively. Following the method given in reference 6, a procedure for applying the variables sampling plan is described below. Figures 9 and 10 illustrate examples of satisfactory and unsatisfactory data quality with respect to the prescribed limits L and U.

The variables sampling plan requires the sample mean difference, $\bar{d}$; the standard deviation of these differences, s_d; and a constant, k, which is determined by the value of p, the proportion of the differences outside the limits of L and U. For example, if it is desired to control at 0.10 the probability of not detecting lots with data quality p equal to 0.10 (or 10% of the individual differences outside L and U) and if the sample size is n = 12, then the value of k can be obtained from Table II of reference 6. The values of $\bar{d}$ and s_d are computed in the usual manner; see table 2 for formulas and a specific example. Given the above information, the test procedure is applied and subsequent action is taken in accordance with the following criteria:

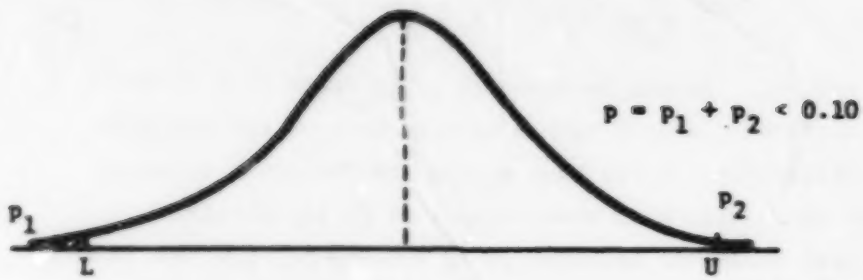


Figure 9. Example illustrating $p < 0.10$ and satisfactory data quality.

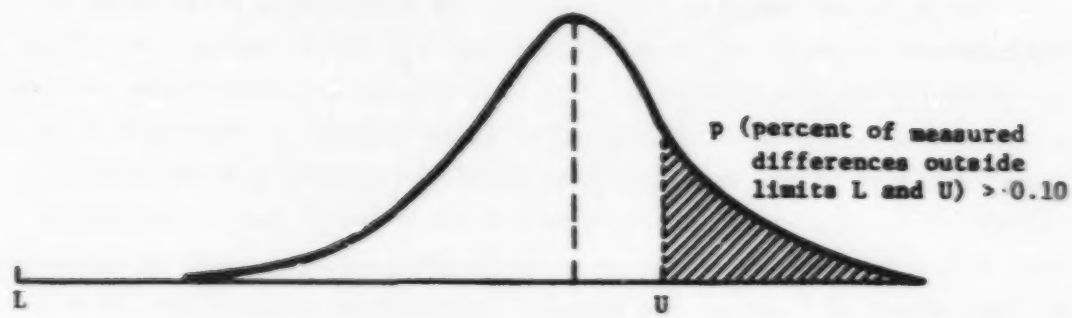


Figure 10. Example illustrating $p > 0.10$ and unsatisfactory data quality.

1. If both of the following conditions are satisfied:

$$\bar{d} - k\, s_d \geq L = -2.86 \text{ mg Pb/ℓ}$$

$$\bar{d} - k\, s_d \leq U = 2.86 \text{ mg Pb/ℓ}$$

the individual differences are considered to be consistent with the prescribed data quality limits and no corrective action is required.

2. If one or both of these inequalities is violated, possible deficiencies exist in the determination process as carried out for that particular lot (group) of determination periods. These deficiencies should be identified and corrected as soon as possible to prevent future determinations of unacceptable quality. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

Table 3 contains a few selected values of n, p, and k for convenient reference.

Using the values of $\bar{d}$ and s_d in Table 2, k = 2.045 for a sample size n = 12, and p = 0.10 (Table 3), the test criteria can be checked; i.e.,

$$\bar{d} - k\, s_d = -0.63 - (2.045)(1.15) = -2.98 < L = -2.86 \text{ mg Pb/ℓ}$$

$$\bar{d} + k\, s_d = -0.63 + (2.045)(1.15) = 1.72 < U = 2.86 \text{ mg Pb/ℓ}$$

Therefore, both inequalities are not satisfied; specifically, the data show a negative bias and are not consistent with the lower limits. The laboratory or field unit responsible for generating these data have not maintained satisfactory quality control activities. The field unit should be notified of the need to improve its data quality. However, the calendar quarter of data or a portion of that quarter of data need not necessarily be invalidated especially if all the gasoline samples analyzed were well below the standard e.g., below 10 mg Pb/ℓ.

The above plan provides a 90 percent probability of detecting lots with 10 percent or more defects (i.e., deviations falling outside the designated limits L and U).

Table 3. Sample plan constants, k for P{not detecting a lot with proportion p outside limits L and U}$\leq$0.1

Sample size n	k(p = 0.2)	k(p = 0.1)
3	3.039	4.258
5	1.976	2.742
7	1.721	2.334
10	1.595	2.112
12	1.550	2.045
13	1.533	2.02
14	1.519	1.999
15	1.506	1.981

SECTION V REFERENCES

1. Standard Method of Rapid Field Test for Trace Lead in Unleaded Gasoline (Colorimetric Method), American Society of Testing and Materials, designation D3348-74.

2. "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

3. D. E. Wagoner , F. Smith and D. E. Gilbert, "Test for Lead in Gasoline by Atomic Absorption Spectrometry," Research Triangle Institute under contract No. 68-02-1234, U. S. Environmental Protection Agency, Washington, D.C. (1974).

4. F. Smith, and A. C. Nelson, Jr., "Measuring Pollutants for Which National Ambient Air Quality Standards have been Promulgated, (Final Report)," Research Triangle Institute under contract No. 68-02-0598, U. S. Environmental Protection Agency, Washington, D.C. (1973).

5. A. Hald, Statistical Theory with Engineering Applications, New York: John Wiley and Sons, 1952.

6. D. B. Owen, "Variables Sampling Plans Based on the Normal Distribution," Technometrics 9, No. 3 (August 1967).

7. D. B. Owen, "Summary of Recent Work on Variables Acceptance Sampling with Emphasis on Non-normality," Technometrics 11 (1969): 639-37.

8. Kinji Takogi, "On Designing Unknown Sigma Sampling Plans Based on a Wide Class of Non-Normal Distributions," Technometrics 14 (1972): 669-78.

9. C. Eisenhart, M. Hastay, and W. A. Wallis (eds.), Techniques of Statistical Analysis, Statistical Research Group, Columbia, University, New York: McGraw-Hill, 1947.

10. E. L. Grant, and R. S. Leavenworth, Statistical Quality Control, 4th ed., St. Louis: McGraw-Hill, 1972.

11. D. A. Simons, Practical Quality Control, Reading, Mass.: Addison-Wesley Publishing Company, 1970, pp. 131-150.

APPENDIX A — FIELD TEST FOR DETERMINATION OF LEAD CONTENT IN UNLEADED GASOLINE

Field Test for Lead (FTL)

Appendix C—Field Test for Determination of Lead Content in Unleaded Gasoline

1. *Scope.*

1.1 This method is intended for use in the field by nontechnical people for the quantitative measurement of lead in unleaded gasoline in the range from 0.01 to 0.10 g Pb/U.S. gal. The method applies to all commercial gasolines and responds to all types of lead alkyls as well as to other organic and inorganic forms of lead.

2. *Summary of Method.*

2.1 The gasoline is treated with iodine and tetraethyl ammonium chloride in chloroform and subjected to ultraviolet light. The lead alkyls form water-soluble lead alkyl iodides, which are removed from the gasoline by shaking it with an aqueous ammonium nitrate solution. The aqueous extract is filtered into a solution of 4-(2-pyridylazo)-resorcinol disodium salt (PAR) and ammonium hydroxide. The lead is determined by measuring its PAR complex colorimetrically at 490 nm using a previously prepared calibration curve.

3. *Apparatus.*

3.1 "Ultraviolet Lamp," long wavelength, 3650 Å, placed in a standard 4-watt fluorescent fixture.

3.2 Measuring Block, aluminum, drilled to hold an 18 by 150-mm test tube, with a mark at a level equal to 5.0 ml of liquid in the test tube.

3.3 "Colorimeter, portable," capable of operating at 490 nm. Any equivalent instrument capable of measurement near 514 nm (the optimum Pb-PAR complex wavelength) may be used.

3.4 "Test tubes" borosilicate, 18 by 150 mm.

3.5 "Pipets," glass, dropping, capable of delivering 2.0 ml with a 2-ml bulb.

NOTE 1: Caution. Gasoline or any of the reagents must not come in contact with rubber. If this happens, discard the bulb and pipet and start again.

3.6 "Funnel," plastic, 2.5 inch inside diameter.

3.7 "Filter paper," ashless, 11.00 cm in diameter.

3.8 "Graduated cylinder," plastic, 10-ml.

3.9 Glass Vials, with caps, disposable, 1-oz. capacity.

4. *Reagents.*

4.1 *Purity of reagents.* Reagent grade chemical shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Ammonium Hydroxide (sp. gr. 0.90)—Concentrated ammonium hydroxide (NH_4OH).

4.3 Ammonium Nitrate Solution (Reagent B)—Dissolve 15.0±0.1 g of ammonium nitrate (NH_4NO_3) in 750 ml of water in a 1-litre volumetric flask. Dilute to the mark with water.

4.4 *Chloroform* ($CHCl_3$).

4.5 *Disodium Salt of 4-(2-pyridylazo) Resorcinol Dihydrate (PAR, $2H_2O$) (Reagent C).* Dissolve 25.0±0.1 mg of PAR in 750 ml of water in a 1 liter volumetric flask. Add 10.0±0.1 ml concentrated NH_4OH. Dilute to the mark with water. Store this in brown bottles out of direct sunlight or in the dark.

NOTE 2: Caution—Low results are obtained if the mono-sodium or unsalted PAR is used in this test.

4.6 *Gasoline, Lead-Free.* Gasoline containing less than 0.001 g PB/gal.

4.7 *Iodine.*

4.8 *Iodine/TEAC/$CHCl_3$ Solution (Reagent A).* Dissolve 1.000 g±1 mg of iodine in 75 ml of chloroform ($CHCl_3$) in a 100-ml volumetric flask. Add 1.000 g±1 mg of tetraethylammonium chloride (TEAC) and mix until dissolved. Dilute to the mark with $CHCl_3$.

NOTE 3: Solutions 4.3, 4.5, and 4.8 have been found to be stable for at least 2 months.

4.9 *Lead Standards.* This method was developed using lead standards prepared by addition of known amounts of various lead alkyls to be blended unleaded gasoline to cover the range of this method.

4.11 *Tetraethylammonium Chloride Monohydrate (TEAC).*

5. *Calibration.*

5.1 Prepare a calibration curve to be used with the portable colorimeter. Such a curve should be prepared as frequently as necessary to assure that accurate test results are being obtained. Use at least four gasoline standards of known lead content that cover the range from 0.01 to 0.10 g Pb/gal. to prepare the curve.

5.1.1 Rinse the 2-ml graduated pipet three times with the gasoline sample. Add 2.0 ml of the sample to a 1-oz glass vial. Add 2.0 ml of iodine/TEAC/$CHCl_3$ solution (Reagent A) from another pipet, to the vial containing the gasoline. Tightly cap the vial.

5.1.2 Place the vial on the ultraviolet light and set the timer to give the sample a 3-minute exposure. *Caution.* Ultraviolet light can be harmful to the eyes. Do not remove any protective shields. DO NOT stare at the light.

5.1.3 After exposure, remove and uncap the vial. Measure 10.0 ml of ammonium nitrate solution (Reagent B) into the 10-ml graduated cylinder. Add this to the vial containing the sample. Recap and shake the vial vigorously for 1 minute.

5.1.4 Place a clean 18-mm test tube in the aluminum measuring block. Add 5.0 ml of PAR solution (Reagent C) to the test tube using the mark on the block such that the upper level of liquid in the tube is equal to the mark on the block. Place the plastic funnel in the test tube. Fold a piece of filter paper and place in the funnel.

5.1.5 When the two layers of liquid in the vial have separated (5.1.3), pour the entire contents of the vial inside the filter paper. The aqueous layer will remain in the filter paper. Tap the funnel to add any remaining drops of aqueous solution to the test tube. Remove the funnel and discard its contents. Swirl the test tube gently using a wrist action to obtain a uniform color.

NOTE 4: The lead-PAR complex formed in 5.1.5 must be measured within 10 minutes after starting 5.1.5.

NOTE 5: A few drops of the organic layer may come through the filter paper. This will not alter the results and can therefore be tolerated. However, if more than 10 drops do come through, refilter the aqueous layer through a fresh filter paper into a clean empty test tube.

NOTE 6: Swirling may cause air bubbles to be trapped in the liquid. Wait for these to settle before continuing. Wipe the test tube off with a clean towel to remove any fingerprints that may be present on the surface of the tube.

5.2 Zero and standardize the colorimeter as follows:

5.2.1 Set the colorimeter at 490 nm. Set zero absorbance (100 percent transmittance) with water in an 18-mm test tube. Read and record the absorbance (or percent transmittance) obtained for the standards prepared under 5.1.5.

5.2.2 Plot the absorbance values versus concentration on rectangular coordinate paper. (If percent transmittance values are used, plot them versus concentration using semilog paper, with the percent transmittance value on the log scale.) Draw a best fit line by eye. When plotting absorbance versus concentration, note that the curve does not pass through the origin.

6. *Procedure.*

6.1 Prepare the sample in accordance with the directions given in 5.1.1 through 5.1.5.

6.2 Place the test tube containing the water in the colorimeter and set the absorbance to zero, or the transmittance to 100%.

6.3 Place the sample in the colorimeter and read the absorbance or percent transmittance.

NOTE 7: *Time limit.* The PAR-lead solution obtained for the sample in 6.1 must be read within 10 minutes after the step described in 5.1.5.

6.4 From the calibration curve, find the lead content of the sample. Determine the lead content to the nearest 0.001 g/gal value.

6.4.1 Round the value obtained in 6.4 to the nearest 0.01 g/gal value. This will be the value reported.

7. *Precision.*

7.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

7.1.1 *Repeatability.* Duplicate results by the same operator should be considered suspect if they differ by more than 0.01 g/gal.

7.1.2 *Reproducibility.* The results submitted by each of two laboratories should not be considered suspect unless the results differ by more than 0.02 g/gal.

APPENDIX B GLOSSARY OF SYMBOLS

This is a glossary of symbols as used in this document. Symbols used and defined in the reference method (Appendix A) are not repeated here.

SYMBOL	DEFINITION
Å	Angstrom
cm^3	Cubic centimeter
cm	Centimeter
gal	Gallon
g	Gram
h	Hour
ℓ	Liter
mℓ	Milliliter
mm	Millimeter
N	Lot size—i.e., the number of determination periods to be treated as a group.
n	Sample size for the quality audit (section 3.3).
nm	Nanometer
P	Phosphorus
r	Repeatability of the measurement method at the 95-percent confidence level.
sp gr	Specific gravity
s_X	Computed standard deviation of a finite sample of measurements (sample standard deviation)
$\bar{X}$	Computed average of a finite sample of measurements (sample mean)
/	Per
μ	Micron
μg	Microgram
$\sigma(X)$	Assumed standard deviation of the parameter X (population standard deviation)
μ_X	Assumed mean value of the parameter X (population mean)
$\hat{\tau}_X$	Computed bias of the parameter X for a finite sample (sample bias)

APPENDIX B GLOSSARY OF SYMBOLS—CONTINUED

SYMBOL	DEFINITION
CL	Center line of a quality control chart.
CV{X}	Coefficient of variation of X, $(100\ \sigma_X/\mu_X)$.
$\bar{d}$	Mean difference between known and measured values of reference samples for n audits.
d_j	The difference in the audit value and the measured value arrived at by the analyst for the jth audit.
K	Tolerance interval constant.
L	Lower quality limit used in sampling by variables.
LCL	Lower control limit of a quality control chart.
P	Percent of measurements outside specified limits L and U (Section 3.4).
Pb	Determined lead in a gasoline sample in mg Pb/ℓ.
Pb_{Tj}	Known value of lead concentration of reference sample j.
Pb_T	True (but unknown) lead concentration of gasoline sample.
Pb'	Known lead concentration of working standard samples.
p{Y}	Probability of event Y occurring.
R	Reproducibility of the determination method.
r	Repeatability of the determination method.
$\bar{R}$	Mean value of the range of samples of size n drawn from a normal population.
s_d	Computed standard deviation of difference between known and measured values.
t_{n-1}	Statistic used to determine if the sample bias, $\bar{d}$, is significantly different from zero (t-test).
U	Upper quality limit used in sampling by variables.
σ_r	Repeatability standard deviation.
σ_R	Reproducibility standard deviation.

APPENDIX B GLOSSARY OF SYMBOLS—CONTINUED

SYMBOL	DEFINITION
$\frac{\chi^2}{f}$	Statistic used to determine if the sample variance, s^2, is significantly different from the assumed variance, σ^2, of the parent distribution (chi-square test).
σ_L	Standard deviation of a parameter determined by two different laboratories.

APPENDIX C GLOSSARY OF TERMS

The following glossary lists and defines the terms as used in this document

Absorbance	The logarithm to the base ten of the reciprocal of transmittance.
Accuracy	A measure of the error of a process expressed as a comparison between the measured value and the true value.
Audit Sample	Sample prepared by the Quality Assurance and Environmental Monitoring Laboratory (concentration unknown to the analyst).
Bias	The systematic or non-random component of system error.
Chain of Custody Label	The seal placed on the container which contains the gasoline sample from the test station.
Control Sample . . .	A standard sample used to check the determination process.
Determination Method	A set of procedures for making a determination.
Determination Process	The process of making a determination including method, personnel, equipment, and environmental conditions.
Liter	Special name for the cubic decimeter.
Lot	A specified number of objects to be treated as a group.
Population	The totality of the set of items, units, measurements, and the like, real, or conceptual, that is under consideration.
Precision	The degree of variation among measurements on a homogeneous material under controlled conditions, and usually expressed as a standard deviation or as a coefficient of variation.

Quality Audit . . . A management tool for independently assessing data quality.

Quality Control Check . . . . . Checks made by the operator on certain items of equipment and procedures to assure data of good quality.

Reference Sample . Sample prepared and certified by the Regional Laboratory or the NBS (concentration unknown to the analyst) for auditing purposes.

Sample . . . . . Objects drawn usually at random from the lot for checking (as used in the section on auditing).

Spectral Bandwidth . . . . . The range of wavelengths between the two points at which the absorbance is one-half the peak absorbance.

Working Standard Sample . . Sample prepared by the Fuel Inspector from a working standard solution to prepare or validate the lead calibration curve.

Working Standard Solution . Solution prepared and analyzed by the Regional Laboratory and supplied to the Fuel Inspector for preparing working standard samples for calibration purposes.

APPENDIX D CONVERSION FACTORS

Conversion factors for converting the U. S. customary units to the International System of Units (SI)* are given below.

TO CONVERT FROM	TO	MULTIPLY BY
absorbance (A)	transmittance (T)	$T = 10^{-A}$
degree Celsius (°C)	degree Farenheit (°F)	°F = (1.8)(°C) + 32
grams (g) of lead/gal	milligrams (mg) of lead/liter	264
milligrams (mg) of lead/liter	g of lead/gal	0.003785
nanometer (nm)	micron (μ)	0.001
	Angstrom (Å)	0.1
	centimeter (cm)	10^{-7}

*Metric Practice Guide (A guide to the use of SI, the International Systems of Units), American National Standard Z210.1-1971, American Society for Testing and Materials, ASTM Designation: E380-70, Philadelphia, Pa., 1971.